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THERMAL DISSOCIATION IN DYNAMIC CONDITIONS BY MODELING THERMOGRAVIMETRIC CURVES USING THE LOGARITHM OF CONVERSION DEGREE

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Abstract

The dependence of conversion degree estimated from the (TG) curve of the mass loss on heating of temperature has been analyzed. It has been shown that dynamic TG curve can be modeled by an equation relating to the logarithm of conversion degree as a function of temperature. A coefficient in the equation developed provides information on the distance from the equilibrium, therefore, the coefficient a_2=0–50 implies equilibrium, while a_2>50 informs about some distance from the equilibrium. Further possibilities for the use of the models of lnα *vs.* $1/T$ in the analyses of thermodynamics and kinetics of thermal dissociation of solids has been shown.

Keywords: calcium carbonate, conversion degree, dependence on temperature, equilibrium conversion degree

Introduction

It is very convenient to discuss the kinetics of the chemical reaction of thermal dissociation of solid:

$$A(s) \rightarrow B(s) + \nu_C C(g),\ \nu_A = \nu_B = 1 \quad (1)$$

using conversion degree. The conversion degree is defined as a molar ratio of the substance of A that is reacted to its initial amount:

$$\alpha \xrightarrow{\text{def.}} \frac{\Delta n_A}{n_{A,i}} \quad (2)$$

For the reaction (1) we can shape a definition (2) into a form which uses the change of mass of the substance A.

$$\alpha = 1 - \frac{m_A}{m_{A,i}} \quad (3)$$

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However, this form is not used often for the description of reaction (1) in which the new solid (B) and gas (C) is formed. This is due to the fact that thermogravimetric profile registers the sum of mass:

$$m = m_A + m_B \tag{4}$$

It is much more convenient to determine the ratio of the mass difference:

$$\alpha = \frac{m_i - m}{m_i - m_f} \tag{5}$$

For reaction (1) Eq. (3) takes a form of:

$$\alpha = \frac{m_{A,i} - m}{m_{A,i} - m_f} \tag{6}$$

where:

$$m_f = m_{A,i}\frac{M_B}{M_A}, \quad M_A > M_B \tag{7}$$

The substitution of (7) for m_f in Eq. (6) gives following form:

$$\alpha = \left(1 - \frac{m}{m_{A,i}}\right)\frac{M_A}{M_A - M_B} \tag{8}$$

Figure 1 shows that for the reaction (1) ($\nu_A = \nu_B = 1$) thermogravimetric curve can be separated into two components describing the reacting substance A and the substance B that is under formation.

$$m_A = \frac{mM_A - m_{A,i}M_B}{M_A - M_B} \tag{9}$$

$$m_B = \frac{(m_{A,i} - m)M_B}{M_A - M_B} \tag{10}$$

Let us observe that for the processes of volatilization, i.e., sublimation, ‘off-distillation’, ($M_A = M_B$) conversion degree is calculated from the thermogravimetric curve by the use of Eq. (5) or (6). However, we cannot use for that purpose the form (8) derived from the definition (2).

It is worth noticing, that the experimental measurement of conversion degree demands the determination of the values of three parameters: m_i, m_f, and m – for each single α point, if we use Eqs (5) or (6). On the other hand, only two parameters, m_i, m, must be known for Eq. (8). That fact is important while analyzing the precision of the experimental determination, especially if there is a need to prove that thermal dissociation have proceed completely or the equilibrium conversion degree ($\dot{\alpha}$) is estimated.

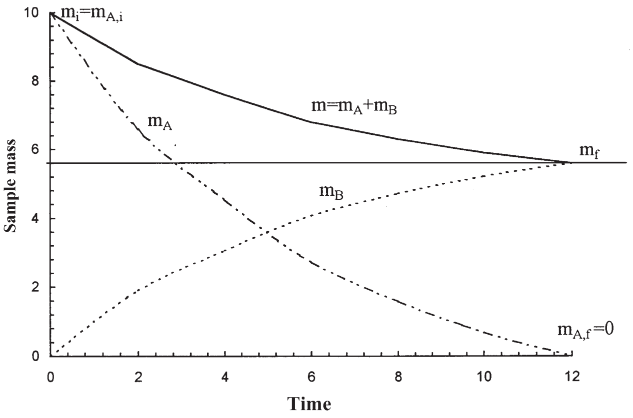


Fig. 1 Mass loss on heating (TG) shown as a sum of the consumption of A and production of B (Eqs (4), (9) and (10))

Basic models

Stiepin and coworkers [1] modified the van't Hoff's isobar to determine the dissociation (or sublimation) enthalpy on the basis of thermogravimetric profiles resulted from the thermal dissociation of solids proceeding according to the scheme (1) for $\nu_C=1$. On the basis of [1] Błażejowski *et al.* [2–15] introduced general equations for $\nu_C>1$ [10–15]:

$$\ln\dot{\alpha}=-\frac{\Delta H_d}{\nu_C R}\left(\frac{1}{T}-\frac{1}{T_p}\right) \tag{11}$$

If: $T=T_p$, $\dot{\alpha}=1$ or in linear form:

$$\ln\dot{\alpha}=-\frac{\Delta H_d}{\nu_C R}\frac{1}{T}+\text{const.} \tag{12}$$

Szarawara *et al.* [16–19] found that for isothermal conditions and low conversion degree the estimation of the activation energy (within 10% accuracy) can be performed by the linearization of the relationship:

$$\ln\alpha=-\frac{E}{RT}+\text{constant},\quad 0<\alpha<\sim 0.2 \tag{13}$$

Equation (13), i.e., so-called temperature criterion, was modified to describe dynamic conditions [20–21]. In such a form Eq. (13) was used [20–21] to verify the kinetic models fulfilling isokinetic effect [20], and *a priori* assumed first order kinetic equation of coal samples [23]. Ortega analyzing this form of temperature criterion [24] proved that Eq. (13) gives a proper value of the activation energy only for the reaction of the *n*-th order processes.

The analysis of the mathematical structure of Eqs (12) and (13) seems to indicate that formally the same relationship describes two different phenomena. As known, the ratio:

$$\eta=\frac{\alpha}{\dot{\alpha}},\quad 0\leq\eta\leq 1 \tag{14}$$

gives the thermodynamic yield of the reaction [19].

If we shape the relationship (14) into a form of:

$$\ln\eta=\ln\alpha-\ln\dot{\alpha} \tag{15}$$

then the dependence of right hand side of (15) on temperature can be analyzed independently.

Analysis of model (11)

For reaction (1) if solid substances A and B do not form solid solutions the van't Hoff's isobar takes a form:

$$\left(\frac{\partial\ln K_{\mathrm{p}}}{\partial T}\right)_{\mathrm{p}}=\frac{\Delta H_{\mathrm{d}}}{RT^{2}} \tag{16}$$

provided that a symbol ° for standard condition is omitted. The equilibrium constant of reaction (1) is given by the Eq. (17):

$$K_{\mathrm{p}}=\left(\frac{\dot{p}}{p}\right)^{\nu_{\mathrm{C}}},\quad p=101.332\ \mathrm{kPa} \tag{17}$$

Usually the conditions of TG measurement do not define the volume of reaction, i.e., volume in which gaseous products are spread. The parameters which are precisely defined are the equilibrium pressure $\dot{p}$ (which depends on the nature of a substance, and is a function of temperature) as well as the atmospheric pressure p if the apparatus is opened to the atmosphere.

In order to describe real thermogravimetric process there is a need for substantial simplifications, therefore, let us make an assumption that V=const. (compare [1] where the authors consider V/RT=const.). Formally, such conditions are fulfilled by a process of the constant volume of gases under constant pressure equaling to 0.1 MPa (1 atm). Therefore, using twicely the gas law we obtain an equation approximating real reaction:

$$\dot{p}V=\nu_{\mathrm{C}}\frac{m_{\mathrm{A,i}}}{M_{\mathrm{A}}}\dot{\alpha}_{\mathrm{A}}RT$$

and

$$pV=\nu_{\mathrm{C}}\frac{m_{\mathrm{A,i}}}{M_{\mathrm{A}}}RT_{\mathrm{p}},\quad \dot{\alpha}_{\mathrm{A}}=1$$

gives:

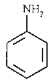
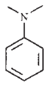
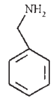
$$\frac{\dot{p}}{p}=\dot{\alpha}_{\mathrm{A}}\frac{T}{T_{\mathrm{p}}} \tag{18}$$

After the omission of the A index ($\alpha_{\mathrm{A}}=\alpha$ for the convenience of notation) Eq. (16) can be given in a form:

$$\frac{\mathrm{d}\ln\left(\dot{\alpha}\frac{T}{T_{\mathrm{p}}}\right)}{\mathrm{d}T}=\frac{\Delta H_{\mathrm{d}}}{\nu_{\mathrm{C}}RT^{2}} \tag{19}$$

provided that the equilibrium state is reached and ΔH_{d}=const.

Table 1 The results of estimation of the parameters of Eqs (12) and (23) for the data given in [8]

A, B and C[a]	Eq. (12)			Eq. (23)			ΔH_{d}/% Eqs (23)–(12)
	ΔH_{d}/ kJ mol^{-1}	const.	r^2/%	ΔH_{d}/ kJ mol^{-1}	const.	r^2/%	
	154.7	20.459	99.96	162.2	27.520	99.96	4.8
	144.7	20.798	99.98	151.3	27.777	99.98	4.6
	195.1	21.947	99.92	203.5	29.173	99.94	4.3

[a] – chemical compounds: aminehydrochlorides data extracted from Table 1 in [8]

After the integration of Eq. (19) in the ranges of $\dot{\alpha}\rightarrow 1$, $T\rightarrow T_{\mathrm{p}}$ we obtain:

$$\ln\dot{\alpha}=-\frac{\Delta H_{\mathrm{d}}}{\nu_{\mathrm{C}}R}\left(\frac{1}{T}-\frac{1}{T_{\mathrm{p}}}\right)-\ln\left(\frac{T}{T_{\mathrm{p}}}\right) \tag{20}$$

Equation (20) differs from this given by a form of (11) only in a term of $-\ln T/T_{\mathrm{p}}$ located on the right hand side. For $T=T_{\mathrm{p}}$, $\dot{\alpha}=1$, because the whole right hand side of Eq. (20) takes a value of 0. Equation (20) involves two coefficients:

$$\ln\dot{\alpha}=a_{\mathrm{o}}-\frac{a_1}{T}-\ln T \tag{21}$$

However, in such a situation that one cannot be certain of if α concerns real equilibrium Eq. (21) can be corrected by the addition of the third coefficient of a_2 to form a relation:

$$\ln\alpha = a_{\mathrm{o}} - \frac{a_1}{T} - a_2 \ln T \qquad (22)$$

Table 1 compares the performance of Eqs (11) and (20) – the latter in a form of Eq. (23):

$$\ln(\dot{\alpha}T) = \frac{-\Delta H_{\mathrm{d}}}{\nu_{\mathrm{C}} R}\frac{1}{T} + \mathrm{constant} \qquad (23)$$

The analysis of the data given in [8] by the use of formula (12) results in the same values of the dissociation enthalpy. On the other hand, the results are 4–5% higher if one uses Eq. (23). In both cases the statistical significance of the correlation obtained is comparable. The parameter estimated referred to the dissociation enthalpy as far as the equilibrium conversion degree is determined experimentally. However, without further thermodynamic analysis we cannot be sure if it is really true.

Analysis of relationship (13)

We take the Ortega interpretation [24] (compare also: Eq. (5) from [24] and (20) from [25]), as the base forming a starting point for further analysis:

$$\ln g(\alpha) = \ln\frac{ZE}{qR} - 5.33 - 1.05\frac{E}{RT} \qquad (24)$$

For the low conversion degrees weight integral $g(\alpha)$ can be substituted for a term obtained from the disintegration of the function into an exponential series. The detailed form of this term depends upon the individual mechanism, which is listed in Table 2.

$$g(\alpha) = a\alpha^{\mathrm{b}}, \quad 0 \leq \alpha \leq {\sim}0.2 \qquad (25)$$

For the $g(\alpha)$ of the F1, R2, R3 and D2, D3, D4 symbols a transformation of the weight integral $g(\alpha)$ to Eq. (25) is performed using the expansion of the Maclaurin's series, while preserving the first term only. For $g(\alpha)$ including the A2 and A3 symbols a term of $[-\ln(1-\alpha)]^{\mathrm{d}}$ is approximated to α^{d}, and for the symbols R1 and D1 there is no need to expend the weight integrals into the series, because $g(\alpha)=\alpha$ and $g(\alpha)=\alpha^2/2$, respectively. The meaning of symbols of the weight integrals discussed has been preserved to comply with this accepted in [21].

From Eqs (24) and (25) we obtain following formula:

$$\ln\alpha = -1.05\frac{E}{bRT} + \mathrm{constant} \qquad (26)$$

The coefficient 1.05 comes from the application of Doyle's approximation of the temperature integral.

Table 2 The expansion of the weight integral $g(\alpha)$ into the exponential series and the corrected values of the activation energy

Symbol of the mechanism	Expansion of the $g(\alpha)$ function into series	$a\alpha^b$ acc. to (25)	E/kJ mol^{-1} calculated		
			in [24]	acc. to (27)	acc. to (27) without 1.05 term
Fn	$\alpha[1+n\alpha/2+n(n+1)\alpha^2/6...]$	α	–	–	–
F1 (n=1)	$\alpha[1+\alpha/2+\alpha^2/3...]$	α	135.2	128.8	135.2
R1 (n=0)	–	α	139.3	132.7	139.3
R2 (n=1/2)	$\alpha[1+\alpha/4+\alpha^2/8+...]$	α	137.3	130.8	137.3
R3 (n=2/3)	$\alpha[1+\alpha/3+5\alpha^2/27...]$	α	136.6	130.1	136.6
A2	–	$\alpha^{1/2}$	272.1	129.6	136.1
A3	–	$\alpha^{1/3}$	408.2	129.6	136.1
D1	–	$(1/2)\ \alpha^2$	69.2	131.8	138.4
D2	$\alpha^2/2[1+\alpha/3+\alpha^2/6...]$	$(1/2)\ \alpha^2$	68.5	130.5	137.0
D3	$\alpha^2/6[1+2\alpha/3+13\alpha^2/27...]$	$(1/6)\ \alpha^2$	67.6	128.8	135.2
D4	$\alpha^2/6[1+12\alpha/27+7\alpha^2/27...]$	$(1/6)\ \alpha^2$	68.1	129.7	136.2

Table 2 showing the results of the modified Ortega approach (compare Table 2 in Ref. [24]) indicates that the temperature criterion given by Eq. (13) if used for the estimation of the activation energy can yield a proper value, provided that index *b* is known. The *b* index can be found quite easily by the trial-and-error method. A few simple calculations allow for the assumption of its value. We use a following proportion for recalculation:

$$E=E_{\mathrm{given}}\frac{b}{1.05} \tag{27}$$

The omission of the coefficient of 1.05 in Eq. (27) gives the results very closely related to those reported in [24], i.e., E=134.2÷136.6 kJ mol^{-1}. The same omission can be performed in Eq. (26), which seems to suggest that (12) and (26) are of the same mathematical structure, while the stoichiometric coefficient ν_C and the *b* index can be seen as the correction terms taking strictly defined values for individual processes, i.e., b=1 for the reaction/process of the *n*-th order, b=2 for the diffusion models from D1 to D4, and the *b* index takes fractional values (b<1) for the mechanisms labeled with A2 and A3.

Modeling of the relationship of the logarithm of conversion degree *vs*. temperature

Thermodynamic approach

In order to decide what is the kind of the dependence of conversion degree upon temperature, it seems reasonable to analyze the thermal dissociation of the substance A that is described in details in the literature. Calcium carbonate can be such a substance that have been studied and described thoroughly by many authors [22, 26–32] and the results are listed in catalogue [33].

We calculate the equilibrium conversion degree taking the thermodynamic data for calcite. Therefore, using the short form of the van't Hoff's isotherm:

$$-RT\ln K_{\mathrm{p}}=\Delta G_{\mathrm{T}}^{\mathrm{o}} \tag{28}$$

we obtain a linear form of the relationship between thermodynamic potential and temperature.

Thermodynamic data extracted from [19] give the following equation:

$$\Delta G_{\mathrm{T}}^{\mathrm{o}}=176072.4-152.13T,\ \mathrm{J\ mol^{-1}} \quad 298\ \mathrm{K}\leq T\leq 1260\ \mathrm{K} \tag{29}$$

to obtain a final form:

$$\ln K_{\mathrm{p}}=-\frac{176072.4}{RT}+18.298;\ T_{\mathrm{p}}=1157.4\ \mathrm{K};\ \Delta H_{\mathrm{d}}=176.1\ \mathrm{kJ\ mol^{-1}} \tag{30}$$

The almost identical relationship results from the experimental data given by Kubas [26]:

$$\ln K_\mathrm{p} = -\frac{173317.8}{RT} + 18.135$$
$$500\,\mathrm{K} \le T \le 1200\,\mathrm{K};\ T_\mathrm{p} = 1149.5\,\mathrm{K};\ \Delta H_\mathrm{d} = 173.3\,\mathrm{kJ\,mol^{-1}} \qquad (31)$$
$$(r^2 = 99.82\%,\ N = 16,\ P = 0.0^{(5)})$$

This relationship covers also some of the data published by Maciejewski [31]. Introducing Eq. (18) into formula (17) we obtain:

$$K_\mathrm{p} = \left(\frac{\dot{\alpha} T}{T_\mathrm{p}}\right)^{\nu_\mathrm{C}},\ \nu_\mathrm{C} = 1 \qquad (32)$$

In this particular case, most of the authors [2–15] simply consider:

$$K_\mathrm{p} = \dot{\alpha}^{\nu_\mathrm{C}} \qquad (33)$$

A discussion on the role of the simplex in Eq. (32) brings to an empirial criterion (22) which will be used in further analysis performed in the current work. The analysis of the experimental data indicates that such an approach can be reasonable – Eq. (23) and Table 1.

In further analysis we use Eq. (30) in the following form:

$$\text{a) } \dot{\alpha} = \frac{1157.4}{T}\exp\left(-\frac{21177.82}{T} + 18.298\right)$$
$$298\,\mathrm{K} \le T \le 1157.4\,\mathrm{K} \qquad (34)$$
$$\text{b) } \dot{\alpha} = 1,\ T \ge 1157.4\,\mathrm{K}$$

Thermokinetic approach

Figure 2 illustrates the conversion degree of the thermal dissociation of $CaCO_3$ taking place in dynamic condition as a function of temperature which is convenient to be presented in a semilog scale. A profile of the equilibrium conversion degree (the one labeled with *0*) was estimated on the basis of Eq. (34). The experimental profiles (*1*, *2*, *3*) resulted from our experiments detailed in Supplement. Profile *4* was scanned from the catalogue [33] – $CaCO_3$ had been obtained from calcium oxalate of the initial mass 724.4 mg – while profile *5* was taken from [30].

Graphical analysis suggests at least 4 possible location of the experimental data in relation to the relationship $\dot{\alpha}$ *vs.* T.

I. The experimental data are located along the $\dot{\alpha}$ *vs.* T profile, i.e., $\alpha \approx \dot{\alpha}$, which is the case for profiles *1*, *2*. Therefore, it can be assumed that linear relationship (11) or (12) should yield the dissociation enthalpy ΔH_d. It is recommended also to make use of Eq. (22) to estimate a value of the experimental parameter a_2.

II. The experimental data are located below the $\dot{\alpha}$ *vs.* T profile, i.e., $\alpha < \dot{\alpha}$, which is fulfilled by profile *3*. In such a case the relationship is of the kinetic type and we can apply typical kinetic equations, e.g., Eq. (24) or temperature criterion (13) better

Table 3 The thermodynamic and thermokinetic analysis of the relationship of the logarithm of conversion degree *vs*. temperature for 5 experiments of thermal decomposition of $CaCO_3$

	Coefficients of Eqs (22) or (36)				
Curve in Fig. 2	I	II	III	R^2/%	*P*
1 air	401.13	$-7.358\cdot10^{4}$	–47.86	99.97	$0.0^{(4)}$
2 argon	327.70	$-6.131\cdot10^{4}$	–38.92	99.88	$0.0^{(4)}$
3 CO_2	31330.15	$-4.673\cdot10^{6}$	–3869.9	99.67	$0.0^{(4)}$
4 data [33]	–1380.61	$+1.487\cdot10^{5}$	178.1	99.98	$0.0^{(4)}$
5 data [30]	1333.83	$-1.858\cdot10^{5}$	–166.26	99.97	$0.0^{(4)}$

	Eq. (12) for $\dot{\alpha}$, criterion (13) for α			
Curve in Fig. 2	ΔH_d or *E*/kJ mol^{-1}	Range of $\dot{\alpha}$ or α	r^2/%	*P*
1 air	(ΔH_d) 186.4	0.03÷0.92	99.63	$0.0^{(5)}$
2 argon	(ΔH_d) 177.0	0.009÷0.989	99.54	$0.0^{(5)}$
3 CO_2	(E) 1306.7	0.065÷0.277	99.70	0.00349
4 data [33]	–	–	–	–
5 data [30]	(E) 239.7	0.004÷0.947	98.58	$0.0^{(4)}$

	Thermokinetic models			
Curve in Fig. 2	Symbol of mechanism	*E*/kJ mol^{-1}	r^2/%	*P*
1 air	–	–	–	–
2 argon	–	–	–	–
3 CO_2	2F1–R1^{a}	1143.3^{a} 1180.8^{b} 1190.7^{c}	99.21 99.19 99.21	$0.0^{(5)}$ $0.0^{(5)}$ $0.0^{(5)}$
4 data [33]	–	–	–	–
5 data [30]	D4	172.4	>99.9	–

a – $g(\alpha)= -\alpha -2\ln(1-\alpha)$, Eq. (24); b – from Eq. (15’), [25]; c – from Eq. (19’), [25] in version (26). Equation (14) gives the thermodynamic yield below 1. Relationship (22) describes feature for such a case: a_2 takes a very large value.

III. The experimental data are located above the $\dot{\alpha}$ *vs.* T profile. The le Chatelier theorem [19]:

$$\frac{\mathrm{d}p}{\mathrm{d}\alpha}\Delta V<0 \tag{35}$$

is satisfied, provided that the intense uptake of the gaseous products takes place. For endothermic reaction (1) $\Delta V>0$, which means a decrease in pressure resulting in the increase of conversion degree, because equilibrium shifts to right obeying relation (14): $0<\eta\leq 1$. For these particular cases we observe high values of the a_2 coefficients.

IV. The experimental data in the function scale, independent of the location in relation to the $\dot{\alpha}$ *vs.* T profile, form an increasing curve of some concavity. The relationship (22) is fulfilled in a version with reversed signs:

$$\ln\alpha=-a_3+\frac{a_4}{T}+a_5\ln T \tag{36}$$

Such a graphical image characterizes the examples of too large initial mass and/or too high heating rate, or completely wrong chosen parameters of the analysis performed. This effect can arouse from the difficulties in the normalization of conversion degree according to the TG curve, which is discussed in the introduction.

Table 3 gives the individual values of the coefficients of Eqs (22) and (36) for the data displayed in Fig. 2. It has been found on the basis of the results of many studies that a value taken by the coefficient a_2 in Eq. (22) is of much importance. Practically, following ranges of a_2 can be separated:

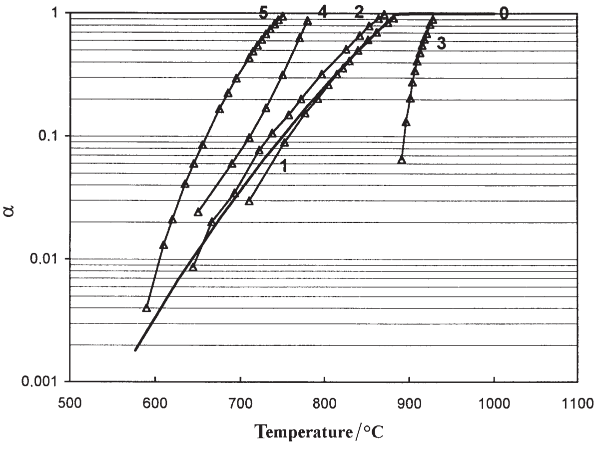


Fig. 2 Dependence of the conversion degree of calcium carbonate *vs.* temperature shown in semilog scale; 0 – the relationship for the equilibrium conversion degree according to (34); 1 – analysis in the air; 2 – analysis in the argon atmosphere; 3 – analysis in the CO_2 atmosphere; 4 – data according to [33]; 5 – data according to [30]

0 – the case characterized by the unambiguous lack of the effect of the term of ln*T*. This approach is illustrated by the publications [2–15],

1 – the case discussed in this work, Eqs (20), (21) or (23), practically ideal equilibrium relationship of type I,

0–50 – the case which can be still classified to type I,

>50 – the example of thermokinetic relationship of type II or III.

This classification is mainly of intuitive nature and cannot be fully verified theoretically, therefore, the criterion (22) and (36) should be considered as nothing more as a kind of indication.

It is shown in Table 3 that for reaction (1), taking place in the most troublesome conditions (CO_2 atmosphere, profile 3 in Fig. 2) among the analyzed models of the kinetic symbols Fn, R1÷3, A2, A3 and D1÷4 or linear combination of R1 and F1 [21–22], the most advantageous result is obtained for the mechanism $f(\alpha)=1-\alpha/(1+\alpha)$, which means weight integral $g(\alpha)=-\alpha-2\ln(1-\alpha)$. A value of activation energy estimated, E=1140÷1307 kJ mol^{-1}, is high but keeps in the range reported by other authors, e.g. E=709÷1558 kJ mol^{-1} [30]. The highest value (E=1307 kJ mol^{-1}) is obtained from the temperature criterion (13) without correction (omitted coefficient 1.05).

A value of dissociation enthalpy estimated from Eq. (12) for thermal dissociation of $CaCO_3$ proceeding under argon: ΔH_d=177.0 kJ mol^{-1}, complies with the ones cited by many authors [31]. The same value is given by Eqs (30) and (31).

Conclusions

The analysis discussed in the current work is based on the study of reaction (1) performed for many model substances. However, the core of the text deals with thermolysis of calcium carbonate. In this work we have assumed that a temperature scale complies with the temperature of the reaction.

Some empirical criteria for the interpretation of the results of reaction (1) in dynamic conditions have been developed.

1. The graphical representation (Fig. 3) of the relation $\ln\alpha$ *vs.* T can shape a profile complying with the empirical formula (22), which is the most common case. It is likely that the patterns described by formula (36) outline unfitted test conditions, mainly too large initial mass of the sample and/or too high heating ratio, or completely inappropriate parameters of the analysis. Case (36) describes the situation of insignificance of the respective relationship of thermodynamic and thermokinetic nature.

2. If one assumes that the empirical model (22) is adequate for the reaction/process, it seems that a_2 from the range 0÷50 practically decides on equilibrium dependence of conversion degree on temperature. In such a case dissociation enthalpy can be estimated by the use of Eq. (11), e.g., in form of (12). Also the significance of Eq. (23) cannot be excluded.

3. The temperature criterion adopted for dynamic condition [20–21] in a form of (13) satisfies the situations defined by conversion degrees ranging from $0<\alpha<0.2\div0.3$. This approach concerns mechanisms of the *n*-th order, as noticed by Ortega [24]. For the

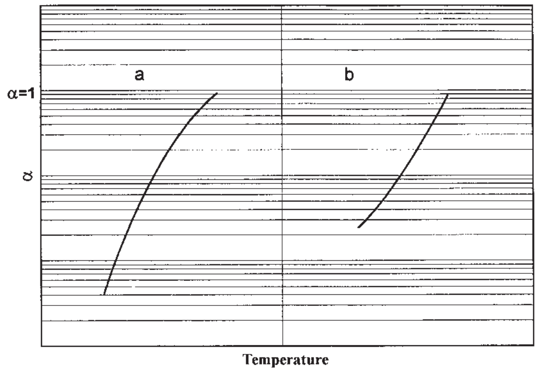


Fig. 3 Relationship of the lnα *vs*. temperature; a – according to Eq. (22) – profile *5*, Fig. 2; b – according to Eq. (36) – profile *4*, Fig. 2

low values of α the criterion can be corrected with the *b* coefficient from Eq. (26). The coefficient *b* takes a value of 1 for the reaction of *n*-th order, $b=2$ for the diffusion models D1÷D4 – and *b* takes a fractional value ($b=1/2$ and $b=1/3$) for the models A2, A3, respectively.

It is recommended to apply a correction for these mechanisms within the criterion (13). The analysis performed showed that a direct correction of activation energy by the use of the *b* coefficient practically yields one value irrespective of thermokinetic model examined (Table 2).

One should not use the criterion (13) or (26) for the situations described by (36).

4. The most difficult for interpretation are cases with linear profiles of lnα *vs*. $1/T$ in the whole range of conversion degree and $a_2=0\div50$. In such a situation temperature criterion (13) is satisfied in a whole range of conversions, however, the relation is closer to Eq. (12), i.e., $\ln\dot{\alpha}$ *vs*. $1/T$. Some other cases obeying this rule can be formed by the kinetics of the 0-th order resulting in R1 mechanism and/or the D1 diffusion model in some sense corresponding to the II Fick's law for a quick processes. This is the case for thermal dehydration of calcium oxalate hydrate, which experimental data were used in [20], $a_2=7.8\div38.2$.

The inconsistency can be explained by the theorem:

$$E\geq\Delta H_{\mathrm{d}} \tag{37}$$

Therefore, the reaction/process in these particular conditions proceeds having the similar values of the activation energy and dissociation enthalpy ($E=\Delta H_{\mathrm{d}}$). The progress of the reaction is controlled by the diffusion processes.

5. In the dynamic processes of thermal dissociation the profile characterizing mass losses (TG or *m*) is shaped by the superposition of at least two rules: van't Hoff's isobar (Clausius-Clapeyron's in the case of volatilization processes) and the Arrhenius equation. The use of the appropriate statistical formalism enable us to separate the individual rule. However, such a formalism is both arbitrary and incompetent in nature, which makes the indisputable identification of the rule difficult. Besides the generally known problems

with the selection of (thermo)kinetic models $g(\alpha)$, some other questions arise. For example the thermolysis of the aniline hydrochloride (the entry 1 of Table 1) can be described both with Eqs (12), (13) and (23), as well as (22). In the latter case the lowest value (in the current publication) of the a_2=1.20 is obtained, but this result is statistically insignificant on level P=0.920.

Supplement

Profiles 1–3 in Fig. 2 have been obtained on the MOM Q1500 D derivatograph under the following conditions: sample: 100.00 mg, atmosphere: air – static (1), argon – dynamic 2.5 cm^3 s^{-1} (2), CO_2 – dynamic 2.5 cm^3 s^{-1} (3), heating rate q=10 K min^{-1}, platinum pots without cover, sensitivity DTA, DTG: 1/10.

The $CaCO_3$ sample was of the analytically pure grade produced by Sojuzchimeksport (Russia) available from POCh Gliwice (Poland).

* * *

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Symbols

a_o, $a_{1.....5}$ – empirical coefficients of the Eqs (22) and (36),
A, B, C – chemical compounds
a, b – coefficients according to (25),
d – exponent (d>0),
E – activation energy/J mol^{-1},
$f(\alpha)$ – symbol of the mechanism of reaction/process,
$g(\alpha)$ – weight integral,
ΔG_T^o – free energy, thermodynamic potential as a function of temperature/J mol^{-1},
ΔH_d – dissociation enthalpy/J mol^{-1},
K_p – thermodynamic equilibrium constant (pressure),
m – mass, i.e., mass loss on heating curve TG/mg,
M – molecular mass,
n – order of reaction,
n_A – number of moles (A),
Δn_A – number of moles reacted (A),
N – number of measurements,
p – vapour pressure or pressure ($\dot{p}$ – equilibrium pressure, p – standard pressure)/kPa,
P – significance level, e.g. $0.0^{(5)} = 0.00000$,
R – universal gas constant, R=8.314 J mol^{-1} K^{-1},
r^2, R^2 – coefficients of the linear and multiplicative determinance, respectively/%,

q – heating rate/K min^{-1},
T – temperature/K, (T_p – temperature for which ΔG^o_T=0),
V – volume/cm^3,
Z – frequency constant in Arrhenius equation/min^{-1},
α – conversion degree, $0\leq\alpha\leq1$,
η – thermodynamic yield, $0\leq\eta\leq1$,
ν – stoichimetric coefficients.

Superscripts

(s), (g) – solid, gaseous, respectively,
· – refers to equilibrium state.

Subscripts

A, B, C – refer to the chemical compounds A, B, C,
i – initial stage,
f – final stage.

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