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Kinetic compensation effect of isoconversional methods

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Abstract

For experimental data obtained under different reaction/process conditions over time or temperature, the kinetic compensation effect (KCE) can be expected. Under dynamic (nonisothermal) conditions, at least two analytical pathways forming the KCE were found. Constant heating rate ($q = \text{const}$) and variable conversion degrees ($\alpha = \text{var}$) lead to a vertical source of the KCE, called the isochronal effect. In turn, for a variable heating rate ($q = \text{var}$) and constant conversion degree ($\alpha = \text{const}$), we can obtain an isoconversional compensation effect. In isothermal conditions (analyzed as polyisothermal), the KCE appears only as an isoconversional source of the compensating effect. The scattering of values for the determined isokinetic temperatures is evidence of a strong influence of the experimental conditions and the calculation methodology. The parameters of the Arrhenius law have been shown to allow the determination of the KCE and further the isokinetic temperature. In turn, using the Eyring equations for the same parameters, we can determine the enthalpy–entropy compensation (EEC) for the activation process and the compensation temperature, which is often treated as an isokinetic temperature. KCE effects have also been shown to be able to be amplified or dissipated, but isokinetic temperature is not a compensating quantity in the literal sense in isoconversional methods because $T_{iso} \rightarrow \infty$. Thus, in isoconversional methods, isoconversional KCE values are characterized by strong variability of activation energy corresponding to the weak variation of the pre-exponential factor, which in practice means that $\ln A \rightarrow \text{const}$. This is completely in line with the classical Arrhenius law.

Keywords Kinetic compensation effect · Enthalpy–entropy compensation · Isoconversional methods · Calcium carbonate

Abbreviations

EEC Enthalpy–entropy compensation
IE Isokinetic effect

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IKR	Isokinetic relationship
KAS	Kissinger–Akahira–Susnose method
KCE	Kinetic compensation effect
NLN	Nonlinear model
OFW (or FWO)	Ozawa–Flynn–Wall method

List of symbols

A	Pre-exponential factor in Arrhenius equation, (min^{-1})
α	Conversion degree, $0 \leq \alpha \leq 1$
D	Derivative in form $\frac{d\alpha}{d \ln T}$, Eq. 18,
E	Activation energy, (J mol^{-1} or kJ mol^{-1})
$f(\alpha), g(\alpha)$	Function depending on the reaction mechanism
H	Enthalpy change of isoentropic reaction/process (J mol^{-1})
ΔH^0	Standard enthalpy (J mol^{-1})
ΔG^0	Standard Gibbs free energy, (J mol^{-1})
k	Reaction rate constant (min^{-1})
N	Number of data
P	Pressure (Pa)
R	Universal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
r^2	Determination coefficient
q	Heating rate (K min^{-1})
q_o	Hypothetical temperature–time relation (K min^{-1})
$Q(u)$	Auxiliary function acc. [40]
s.l.	Significance level
ΔS^0	Standard entropy ($\text{J mol}^{-1} \text{K}^{-1}$)
T	Absolute temperature (K)
φ	Simplex of entropies
τ	Time (min)

Subscripts

c	Compensation state
eq	Equilibrium value or state
f	Final value or state
i	Initial value or state
iso	Isokinetic value or state
j	Selected experimental point
o	Standard condition
*	Thermodynamic function of activation

Introduction

The temperature dependence of the reaction rate for many chemical processes is normally described by the Arrhenius equation, typically expressed by the relationship:

$$k = A \cdot \exp\left(\frac{-E}{RT}\right) \quad (1)$$

The coefficients of Eq. 1 form a linear relationship. Due to coefficients depending on both mathematical factors (selection of kinetic equations) and chemical similarity, the variability of coefficients occurs. This variability of coefficients is known as the kinetic compensation effect (KCE); it is sometimes rarely known as the isokinetic effect (IE) or the isokinetic relationship (IKR).

However, two associated concepts should be distinguished. From a thermodynamic point of view, the kinetic compensation effect (KEC) derives from the basic equation of the Gibbs standard free energy ($\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$), although this relationship is difficult to demonstrate directly. According to [1], the interpretation brought to the definition of the enthalpy-entropy compensation relationship for specific thermodynamic functions is the most important in this case. Therefore, we distinguish two groups of approaches in the literature: by ΔH° vs. ΔS° [2–11] as well as ΔH° vs. $(-T)\Delta S^\circ$ for $\Delta G^\circ = \text{const}$ [12–14]. As a result of cyclical discussions initiated by Starikov et al. [2–7, 14] explains the concept of the enthalpy change in the iso-entropic reaction/process. The analytical relationship between the EEC and KCE shall be demonstrated by the activation functions generally attributed to Eyring. These considerations are evident due to the analytical relationship between the kinetic constant and thermodynamic functions of activation [15–19]. The encyclopedia [1] comes with a case of a generally known compensation effect only for catalytic reactions, which describe the kinetic (isothermal processes) or thermokinetic studies (dynamic processes).

From the point of view of kinetics, the chemical similarity of the substrates, variability of conditions and the formal reaction/process model affect the relationship between enthalpy and entropy. Hence, a comparative analysis of the KCE and EEC effects seems indispensable for understanding the course of the reaction/process.

Based on selected literature data, the results for the thermal decomposition of calcium carbonate (calcite) obtained by different authors for a number of years has shown that the isokinetic temperature covers a wide range $T_{iso} = 815\text{--}1250$ K [20–26].

Theoretical background and aim of this work

According to the insightful papers [27, 28] based on the mathematical source of the relationship:

$$\ln A_j = \ln k_{iso} + \frac{E_j}{RT_{iso}} \quad (2)$$

Barrie performed multivariate calculations regarding the effect of random experimental errors [27] and of systematic errors [28]. Discussion of the isoconversional methods for determination of kinetic parameters since 2000 [29] have become the most commonly used [30–33] and have created the opportunity to perform KCE analysis for variable conditions.

However, the achievements of the ICTAC conference [29, 34–37] and further studies analyzing its results [31–33] do not consider the issues of the KCE or the EEC. An exception is paper [26], which tackles this problem. The many factors influencing differences in kinetic parameters obtained from the same experimental data sets were noted in this work. This situation can be understood with respect to the objections associated with errors [27, 28, 38] and the lack of clarity in the value of coefficients in KCE Eq. 2. Thermal decomposition of chemical compounds (di-tert-butyl peroxide) under different conditions may be an appropriate example [39].

The possibilities to compare the results obtained under dynamic and isothermal conditions are also created. In the dynamic methods, a constant linear temperature increase is the most often applied. Hence:

$$q = \frac{dT}{d\tau} = \text{const} \quad (3)$$

The differential kinetic equation:

$$\frac{d\alpha}{d\tau} = A \cdot \exp\left(\frac{-E}{RT}\right) \cdot f(\alpha) \quad (4)$$

After considering Eq. 3, it is converted to the form:

$$\frac{d\alpha}{dT} = \frac{A}{q} \cdot \exp\left(\frac{-E}{RT}\right) \cdot f(\alpha) \quad (5)$$

In addition:

$$g(\alpha) = \frac{A}{q} \int_0^T \exp\left(\frac{-E}{RT}\right) dT \quad \text{where} \quad g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} \quad (6)$$

The integral on the right-hand side of Eq. 6 called the temperature or Arrhenius integral can be approximated by 25 solutions using an auxiliary function $Q(u)$ [40]. In consequence, there are also numerous isoconversional methods. In practice, the simplest integral equations are the best known, among others KAS, OFW (or FWO), NLN [30, 31, 41], or a more complicated Vyazovkin's method [30, 31, 42–46], but these equations lead to considerable incorrectness in the case of variable activation energy [47].

The fixed conversion degree, i.e., $\alpha = \text{const}$, is assumed in isoconversional methods. The use of several different constant heating rates according to Eq. 3 and $q = \text{const} > 0$ is the fundamental issue in these methods. The heating rate equals $q = 0$ under isothermal conditions; however, if the experiments are repeated at several different temperatures, these conditions are referred to as polyisothermal conditions, forming an experimental matrix $[\tau \times T]$ [48].

Not many studies report on the comparison of the results obtained under isothermal and dynamic conditions. These issues were analyzed by Holba and Šesták [49], Vyazovkin and Wight [44] and at the conference [29]. An interesting proposal in this field is also presented in study [50].

Despite many objections, especially in the category of reliability of isokinetic temperature T_{iso} determination, the work is aimed at demonstrating that the KCE can be a useful tool for qualifying different solutions of kinetic equations, both under isothermal and dynamic conditions. The main interest is focused on the differences in values for coefficients of linear Eq. 2 in the context of their physical meanings. According to [1], isokinetic temperature T_{iso} refers to the Gibbs free energy of activation. A broader definition is also used in the literature for the temperature of compensation associated with the EEC [2, 4–8, 10, 15] as well as with the KCE [7]. In this paper, isokinetic temperature is defined by Eq. 2, but the discussion also concerns the temperature of compensation.

Kinetic models

The results of the thermal decomposition of calcite (CaCO_3), which are discussed in detail in [29], were used for our considerations. Detailed sets of experimental kinetic data were obtained from Prof. M. Brown (Chem. Dept., Rhodes Univ. Grahamstown, South Africa 6140). This paper presents the results of kinetic analysis of four sets of experimental data: two sets obtained under dynamic conditions at several different constant heating rates and two sets obtained under isothermal conditions at several different temperatures in a vacuum and in a nitrogen atmosphere, respectively.

According to Eq. 6, there is a necessity to establish a specific form for both the left and right side of this equation (Table 1).

Based on theoretical considerations, the F1 model is preferred in [51]. Hence, for further calculations, the following form of the integral functions $g(\alpha)$ was assumed: first order kinetics $g(\alpha) = -\ln(1 - \alpha)$. The right side of Eq. 6 is considered below.

Dynamic conditions

In accordance with the reasons specified in [50], which was based on the earlier work [52], the following equation was adopted to the considerations:

$$g(\alpha) = \frac{A}{q} e^{\left(\frac{-E}{RT}\right)} (T - T_i) \quad (7)$$

Equation 7 was adopted bearing in mind the possibility of using one equation to analyze data obtained under various experimental conditions, including isothermal (see Eq. 11). An additional advantage of Eq. 7 is that it is not necessary to use approximate solutions of the temperature integral (Eq. 6) for the example given in [40].

Equation 7 creates two types of KCE depending on the coordinate system selected $[g(\alpha_j), T_j]$, where T_j is an independent variable, $T_j \equiv T$.

The equations 8 are the source of vertical KCE recurring at regular intervals, therefore called isochronal:

Table 1 Analysis conditions for four sets of experimental data considered in this paper

Parameter	Conditions			
	Dynamic/hydrogen	Dynamic/vacuum	Isothermal/nitrogen	Isothermal/vacuum
Temperature T, K	0.1–0.9 step 0.1 –	0.1–0.9 step 0.1 –	0.1–0.9 step 0.1 973.15; 983.15; 992.15; 1005.15; 1013.15; 1023.15; 1043.15	0.1–0.9 step 0.1 788.15; 793.15; 803.15; 808.15; 813.15; 823.15
Heating rate q, K min ⁻¹	1.0; 3.0; 5.0; 7.5; 10.0; 15.0; 25.0	1.8; 2.5; 3.5; 5.0; 6.2; 10.0	–	–
Number of data points, N	9 × 7 = 63	9 × 6 = 54	9 × 7 = 63	9 × 6 = 54
Equations used	Equations 8, 9 and 10	Equations 8, 9 and 10	Equation 12	Equation 12

$$\ln \frac{g(\alpha_j)}{T_j - T_i} = \ln \frac{A}{q} - \frac{E}{RT_j} \quad \text{when } q = \text{const} \quad \text{and} \quad g(\alpha_j) = \text{var} \quad (8)$$

The term isochronal KCE was adopted because of its source, i.e., the degree of conversion is a monotonic increase with time under isothermal conditions or with temperature at a constant heating rate under dynamic conditions.

The horizontal KCE occurs when Eq. 9 is considered ($T_j \equiv T$):

$$\ln \frac{q}{T_j - T_i} = \ln \frac{A}{g(\alpha_j)} - \frac{E}{RT_j} \quad \text{when } g(\alpha_j) = \text{const} \quad \text{and} \quad q = \text{var} \quad (9)$$

In this case, we assumed that a constant degree of conversion considered independently of time or temperature (for isothermal or dynamic conditions, respectively) is the source of the horizontal, called as isoconversional KCE.

The proper selection of the kinetic function $g(\alpha)$ in the form of $g(\alpha_j)$ in Eq. 9 does truly matter. Adopting a specific kinetic function unambiguously determines the value of A , because their ratio is a constant value.

After recombination of Eqs. 8 and 9, one can obtain the relationship:

$$\ln \frac{q \cdot g(\alpha_j)}{T_j - T_i} = \ln A - \frac{E}{RT_j} \quad (10)$$

Fig. 1 presents the KCE resulting from the demonstration that under dynamic conditions: isochronal (according to Eq. 8, Fig. 1a), isoconversional (according to Eq. 9, Fig. 1b) and their recombination (according to Eq. 10, Fig. 1c), KCE occurs.

The source of systematic errors under dynamic conditions may result from the commingling of the relationship between Eqs. 8 and 9 and establishing the relation in Eq. 10 with highly dispersed experimental points.

Isothermal conditions

Under isothermal conditions, the integral form directly resulting from Eq. 4 is commonly used and takes into consideration the integral function given in Eq. 6:

$$g(\alpha) = A \cdot e^{\left(\frac{-E}{RT}\right)\tau} \quad (11)$$

The isoconversional KCE resulting from Eq. 11 is observed under polyisothermal conditions for isoconversional methods (Fig. 2):

$$\ln \frac{g(\alpha_j)}{\tau} = \ln A - \frac{E}{RT} \quad \tau > 0 \quad g(\alpha_j) = \text{const} \quad (12)$$

Fig. 3 shows that $\ln A$ and E linearly increase with the degree of conversion that indicates that activation energy depends on the degree of conversion.

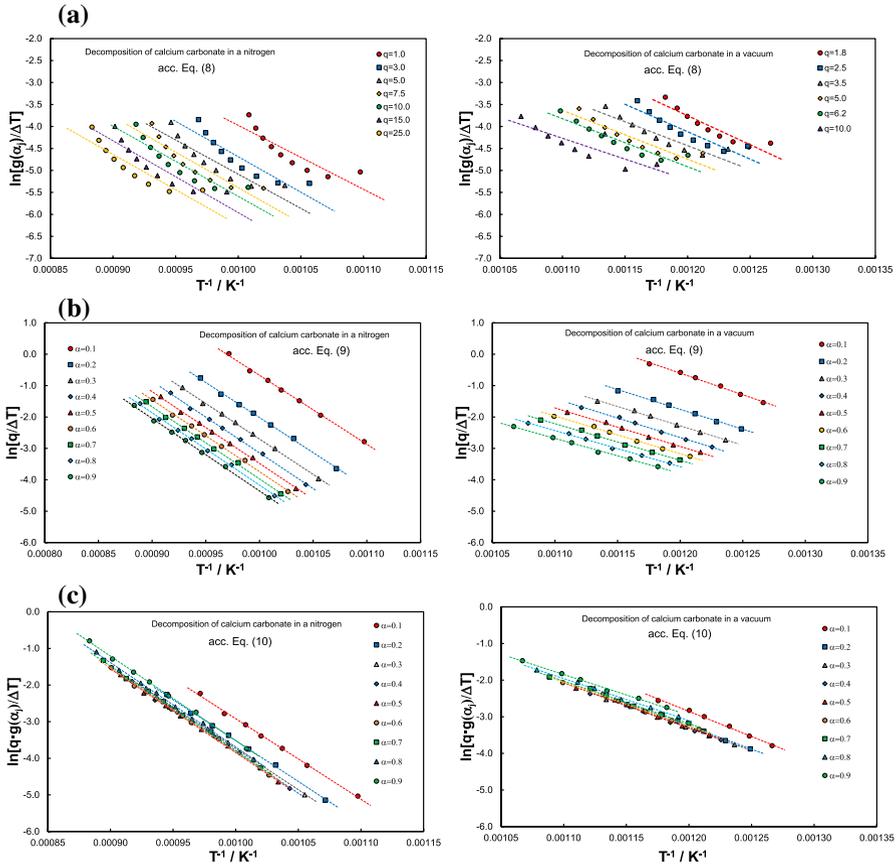


Fig. 1 Experimental data analyzed according to: **a** Eq. 8, **b** Eq. 9 and **c** Eq. 10 $\Delta T = T_j - T_i$

If the experiment is carried out at different temperatures (polyisothermal conditions) and the time and temperature are treated as variables, then the relationship between them can be written in the hypothetical form but without physical meaning, with a temperature–time relationship similar to the definition of the heating rate:

$$q_0 = \left(\frac{\partial T}{\partial \tau} \right)_{g(\alpha_j)} \tag{13}$$

Rearranging Eq. 11 and after differentiation with respect to time and temperature, we can demonstrate:

$$q_0 = \frac{dT}{d\tau} = -\frac{RT^2}{E\tau} \quad g(\alpha_j) = \text{const} \tag{14}$$

Equation 14 can be written in reverse form:

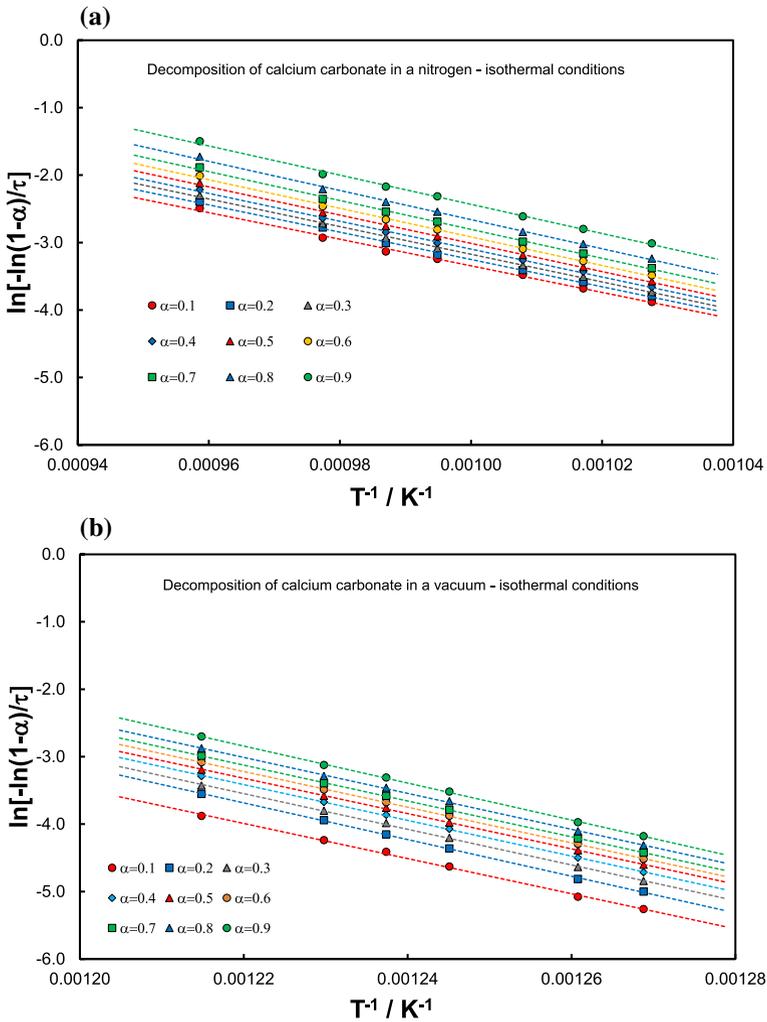


Fig. 2 Polyisothermal data analyzed by isoconversional method according to Eq. 11 create a series for $g(\alpha_j) = \text{const}$: **a** decomposition of calcium carbonate in a nitrogen, **b** decomposition of calcium carbonate in a vacuum

$$\frac{d\tau}{dT} = -\frac{E\tau}{RT^2} \tag{15}$$

This is transformed into differential form:

$$d \ln \tau = \frac{E}{R} d\left(\frac{1}{T}\right) \quad \tau > 0 \quad g(\alpha_j) = \text{const} \tag{16}$$

In the relationship $\ln \tau$ vs. $1/T$, the slope determines the activation energy, which is dependent on the degree of conversion. In the specific case for finite

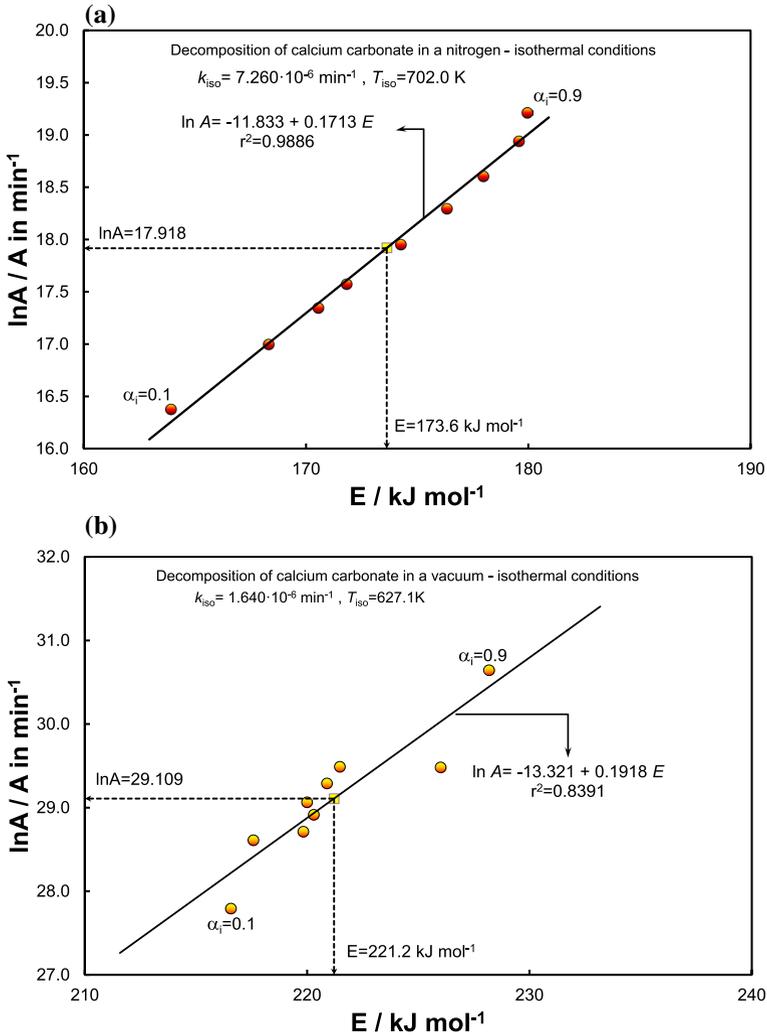


Fig. 3 The isoconversional KCE for the isoconversional method for the experiment performed under polyisothermal conditions: **a** decomposition of calcium carbonate in a nitrogen, **b** decomposition of calcium carbonate in a vacuum (square point— $\ln A$ and E determined from all data for all conversion degrees)

time, the considerations are still valid [50, Eq. 24]. This approach is noted in Vyazovkin's earlier studies [45, Eq. 5], [31, Eq. 3.6].

Equation 12 represents the linear form resulting from Eq. 16, and thus the intercept in this equation is expressed as: $-\ln\left(\frac{A}{g(\alpha_j)}\right)$ when $\tau = \tau_j$. Thus, under the polyisothermal conditions, the existence of KCE is inevitable.

Discussion

Selection of the kinetic model

In the considerations presented, the selection of the kinetic model is very important. It is easy to notice that the origin of Eq. 7 under dynamic conditions considering Eq. 3 leads to Eq. 11 adopted for isothermal conditions. For reactions under dynamic conditions, time τ in Eq. 7 can be expressed as $\tau = \frac{T-T_i}{q}$ (or $\tau = \frac{T}{q}$ in [53]), and it is the reaction time of an actually observed reaction in the range of $\alpha > 0.05$. Therefore, under dynamic conditions we omit the time in which the sample warms up, and the mass changes are not very significant. According to the theoretical considerations presented in [53], this stage of the process to the isokinetic temperature called "elbow" or "kness" has a great cognitive significance but mainly due to the technical and measuring reasons generally omitted. Formally, the integration range from $T_i = 0$ is usually adopted.

KCE with regard to T_{iso}

According to [53] the reaction rates of solids dissociation measured at constant temperature (isothermal) and constant heating rate (nonisothermal) are equal at the isokinetic temperature T_{iso} . This definition makes it possible to assign isokinetic temperatures to many kinetic models for the $\alpha_{iso} < 0.05$ coordinate.

Thus, the definition of isokinetic temperature according to [53] under dynamic conditions truly corresponds to the temperature of the step growth of the reaction/process rate. As a consequence, we observe for $T \leq T_{iso}$, $0 < \frac{d\alpha}{dT} \leq \frac{1}{T_{iso}}$ and $\frac{d\alpha}{dT} \gg 0$ for $T \geq T_{iso}$, what results from the relationship:

$$\left(\frac{d\alpha}{dT}\right)_{T_{iso}} = \frac{1}{T_{iso}} \quad (17)$$

Equation 17 is a special case of derivative $D \equiv 1$:

$$D = T \frac{d\alpha}{dT} = \frac{d\alpha}{d \ln T} \equiv 1 \quad (18)$$

The isokinetic temperature can be determined using the kinetic equation for dynamic conditions and the Eq. 1, from which we create the expression satisfying the condition in Eq. 18:

$$D = \frac{kT_{iso}}{q} f(\alpha_{iso}) = 1 \quad (19)$$

For the thermal decomposition of CaCO_3 discussed in [29], assuming according to Anderson the values: $E = 191 \text{ kJ mol}^{-1}$, $\ln A = 15.4$ (A in min^{-1}) and the zeroth order kinetics $f(\alpha) = 1$, the coordinates $T_{iso} = 955.06 \text{ K}$, $\alpha_{iso} = 0.0416$ for $q = 10 \text{ Kmin}^{-1}$ were found by an iterative method. The isokinetic temperature

determined in this way should be regarded as the initial measurable point of kinetic examination. Based on the interpolation of many literature values and our own data, we can conclude that the isokinetic temperature T_{iso} takes lower values than the equilibrium temperature T_{eq} . The exception is data obtained by isoconversional methods under dynamic conditions. In this study, for $\alpha = 0.05$, the experimentally determined isokinetic temperature for the four cases analyzed is in the range: 894.95 K to 1043.15 K (N_2) and 781.29 K to 837.11 K (vacuum).

As mentioned previously, depending on the methodology used to perform tests and the interpretation of those tests (isothermal and dynamic conditions, selected experimental results), the isokinetic temperature for thermal decomposition of calcium carbonate varies in the range 815–1250 K [20–26].

Fig. 4 shows the intersection of two straight lines generated from Eqs. 8 and 9 and two points with coordinates (E , $\ln A$), the first point calculated from Eq. 10 and the second point based on isothermal data. The kinetic parameters calculated for the decomposition of calcium carbonate under dynamic and isothermal conditions in the nitrogen atmosphere, as well as the coordinates of the intersection of the straight lines, have similar values (Fig. 4a). However, in the case of decomposition in a vacuum, the calculated kinetic parameters are significantly different (Fig. 4b). The straight lines estimated according to the equations for the dynamic method (Eqs. 8 and 9) may intersect, determining a common pair (E , $\ln A$). Other pairs (E , $\ln A$) coming from isothermal calculations are also placed on these straight lines.

Values of isokinetic temperature obtained in the considerations from isodynamic, isoconversional, and isothermal KCE are, respectively, 2625 K, 716 K, and 702 K for experiments in a nitrogen atmosphere ($T_{iso} = 2625 \text{ K} \gg T_{eq}$) and 810 K, 1122 K, and 627 K for experiments carried out in a vacuum. The determination coefficients for the straight lines shown in Fig. 4, with the exception of $r^2 = 0.3401$ (s.l.=0.1), are statistically significant (significance level s.l.=0.001). Analyzing the experimental data (E , $\ln A$) presented in [29] (see Fig. 5), isokinetic temperatures were calculated for the process carried out in a nitrogen atmosphere ($T_{iso} = 751.7 \text{ K}$), in a vacuum ($T_{iso} = 918.2 \text{ K}$) and all data together ($T_{iso} = 786.1 \text{ K}$). All calculated isokinetic temperatures are lower than the temperatures determined according to Eq. 19 on the basis of data [29] ($T_{iso} = 955.06 \text{ K}$).

Certainly, a novelty is the determination of the isokinetic temperature according to [53], which is described by Eqs. 17–19, which suggests the experimentally determined start of the reaction/process.

KCE as a source of EEC

The enthalpy-entropy compensation is observed in the case of:

- testing a series of chemical reactions and many physicochemical processes,
- single reaction/process mathematical formalism analysis.

For thermodynamic activation functions, the EEC equation is determined from kinetic data for the active complex, i.e., from the estimated parameters of the

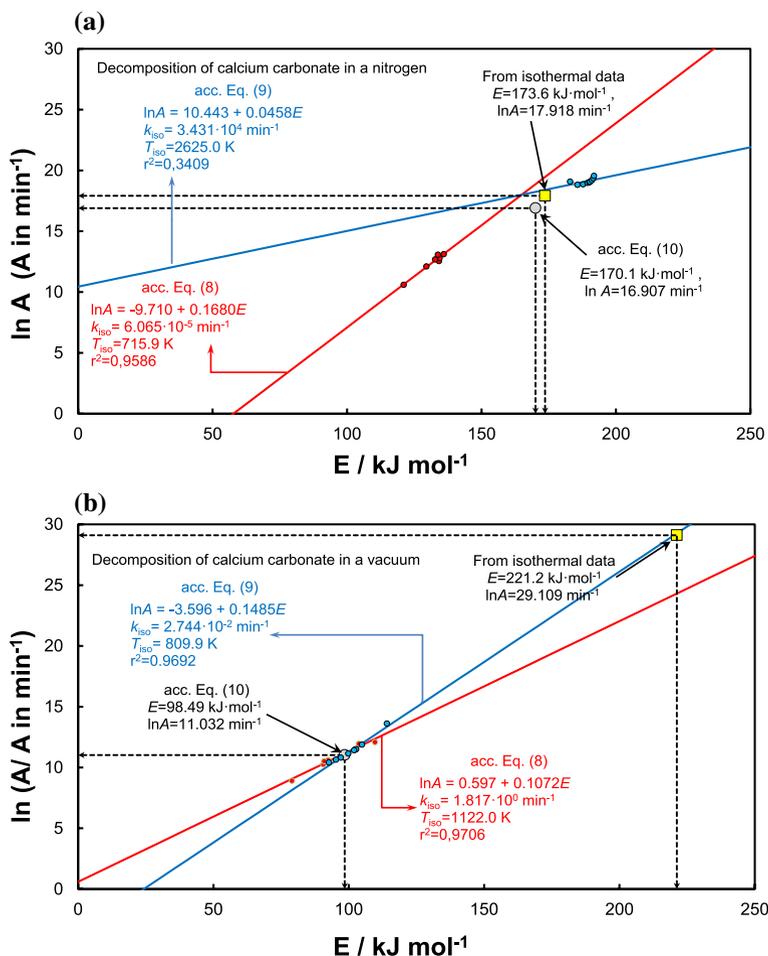


Fig. 4 Comparison of the KCE generated from Eqs. 8–9 and point $(\ln A, E)$ calculated from Eq. 10 **a** decomposition of calcium carbonate in nitrogen atmosphere, **b** decomposition of calcium carbonate in a vacuum (yellow points $E, \ln A$ were determined on the basis of isothermal data—Fig. 3)

Arrhenius equation $(E, \ln A)$ and the temperature of the maximum reaction rate. Based on $N = 30$ data presented in [54] and the most reliable $N = 4$ data presented in [22], the relationship was determined for three kinetic models (D2, D4, R2) (Fig. 6):

$$\Delta H^* = 1164.6\Delta S^* + 342.22 \cdot 10^3 \quad (r^2 = 0.9942) \quad (20)$$

The slope in Eq. 20 is the compensation temperature $T_c = 1164.6\text{K}$, which (for the analyzed data [22, 54]) is very close to the theoretical equilibrium temperature of the chemical reaction $T_{eq} = \Delta H^\circ / \Delta S^\circ = 1172.4\text{K}$ [55].

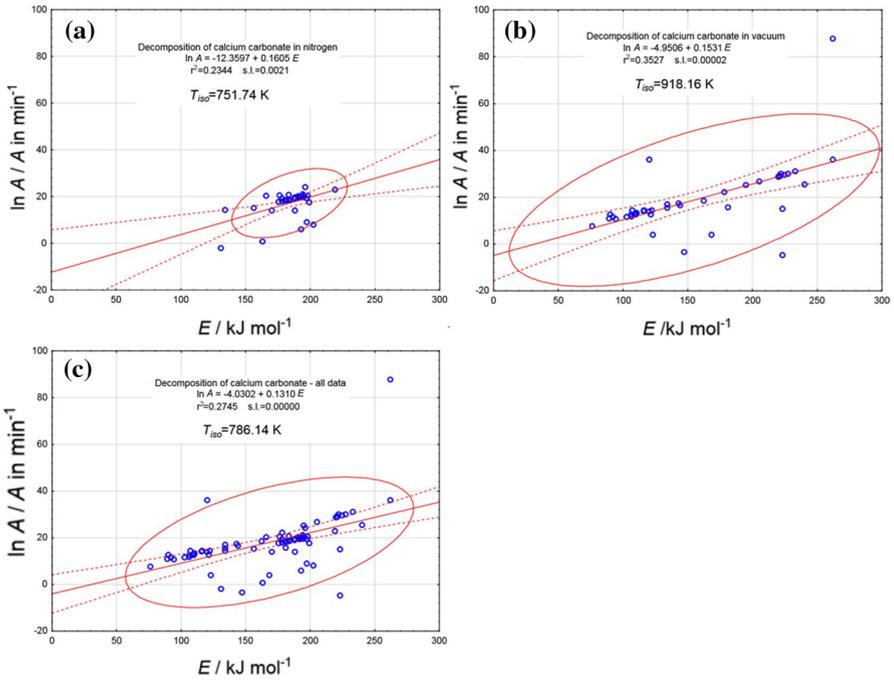


Fig. 5 The KCE and confidence ellipses for kinetic parameters of thermal decomposition of calcium carbonate determined by different authors [29]; kinetic parameters for: **a** nitrogen atmosphere, **b** vacuum, **c** all data

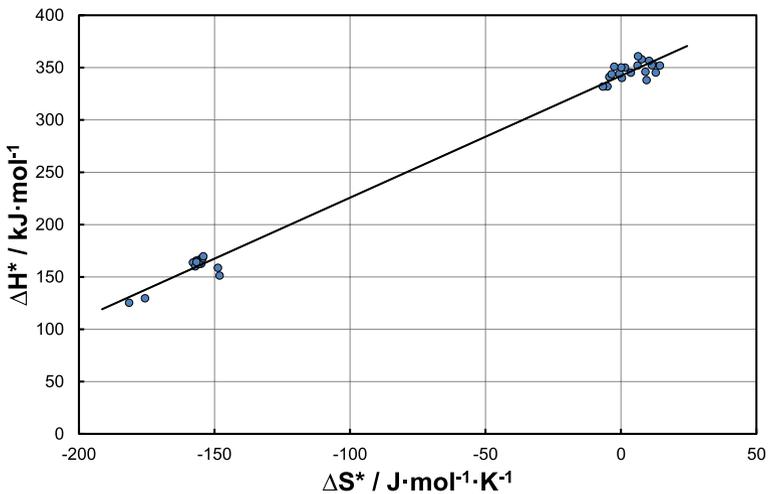


Fig. 6 EEC as result of the relationship between enthalpy and entropy of activation

If the compensation effect is the result of measurements carried out for a series of chemical reactions or many physicochemical processes (case a)), then the slope of Eq. 20 is often referred to as the isokinetic temperature [1, 17–19]. At this temperature, all the members of the series have the same rate constant. The compensation temperature determined here is the result of comparing various reaction mechanisms expressed by the kinetic functions.

If we assume that $T_c \rightarrow T_{eq}$, then Eq. 20 in the generalized form can be written as:

$$\frac{\Delta H^* - H}{\Delta S^*} = \frac{\Delta H^\circ}{\Delta S^\circ} = \text{const}, \quad \Delta S^* \neq 0 \quad (21)$$

According to Starikov et al. [2–7, 14], enthalpy marked as H is called enthalpy change of isoentropic reaction/process, and according to [19], it refers to a hypothetical reaction/process.

The relationship of Eq. 21 connects thermodynamic activation functions with phenomenological functions and as follows from Eq. 20 is equal to: $H = 342.22 \text{ kJmol}^{-1}$.

For the course of a finite reaction/chemical process, the right side of Eq. 21 assumes a constant value. However, on the left side, depending on the mechanism initiated by the change of the activation entropy ($\Delta S^* \neq 0$), there must be a change in the activation enthalpy. The direction of these changes depends on the value of the difference ($\Delta H^* - H$), i.e., whether it is greater or less than zero, and this in turn depends on the sign of the activation entropy. For $\Delta S^* = 0$, Eq. 21 no longer makes sense, but EEC in the form of Eq. 20 is still valid, since $H = \Delta H^*$.

For these reasons, it is more convenient to write:

$$H = \Delta H^* - \varphi \Delta H^\circ = \text{const} \quad \text{where } \varphi = \frac{\Delta S^*}{\Delta S^\circ} \quad (22)$$

From Eq. 22, it follows that for $\Delta S^* = 0$, $\varphi = 0$, and then $H = \Delta H^*$.

Both parts of Eq. 22 are variable, but their difference is a constant value. The more negative values for ΔS^* show that its structure is far from its own thermodynamic equilibrium compared to CaCO_3 . The simplex value φ is close to ± 1 . If we assume the variability of ΔS^* , which is usually in the range of $\pm 150 \text{ J mol}^{-1} \text{ K}^{-1}$ [18], then for $\varphi = -1$ according to Eq. 22, we note very large opportunities for energy compensation. Approximately according to Eq. 22 $H = 150 + 170 = 320 \text{ kJ mol}^{-1}$, and the value is close to the intercept in Eq. 20. For $\varphi = 1$, $H \rightarrow 0$, $\Delta H^\circ = 170 \cdot 10^3 \text{ J mol}^{-1}$ [55], so the system is heading towards the equilibrium temperature. This temperature is closer to the end of the reaction/process, and above it, the reaction is irreversible.

The above considerations show some kind of the possibility of substitution. The parameters of the Arrhenius law allow the determination of KCE and, further, the isokinetic temperature. In turn, using the Eyring equations from the same parameters, we can determine the EEC for the activation process and the compensation temperature, which is often treated as the isokinetic temperature.

Even a very high KCE correlation does not guarantee the correctness of the determined isokinetic temperature for the assumed reaction/process. By analyzing the identical reaction/process but for different ranges of variation of the degree

of conversion, $\alpha = \text{const}$ or var , we can obtain new pairs of E and $\ln A$, which will determine new parameters of the KCE or EEC equation. Thus, for the same reaction/process, the isokinetic temperature identification is derived from the adopted experimental conditions and mathematical formalism.

The scattering of the determined isokinetic temperatures is evidence of a strong influence of the experimental conditions and the calculation methodology.

Very high values of isokinetic temperatures were obtained for the isoconversion kinetic compensation effect, which may indicate that the isoconversional KCE contributes to the greatest error of the values determined for the kinetic parameters. The isokinetic temperatures determined based on polyisothermal studies are less than the range values determined by the isochronal and isoconversional KCE.

The temperature determined should not be regarded as "absolute truth". When drawing conclusions based on compensation effects, we should consider that they may constitute a kind of pitfall. As demonstrated by Lente in his book [18], they can lead to the fallacy of kinetic parameters.

KCE in the context of isothermal and dynamic measurements

Variability of kinetic parameters, which is the result of kinetic and thermokinetic considerations, should be considered from the point of view of experimental conditions (experimental realities). Analyzing the course of the reaction/process in dynamic or isothermal conditions, we assume that they have a finite character, i.e., we can determine the beginning and the end.

It is also possible to implement observations obtained under dynamic conditions to isothermal measurements relative to the equilibrium degree of reaction [49] in the form of the equation currently called the Holba–Šesták equation (the geometrical sense is shown in Fig. 6 in [49]).

In the case of isoconversional methods, both for isothermal and dynamic conditions, we assume that the process starts ($0 < \alpha < 1$), and analysis is performed for constant values of $\alpha = \text{const}$ for increasing values of time and/or temperature.

It is especially important when we do not consider very important measurements in terms of the slowly changing degree of conversion below the isokinetic temperature according to Lyon [53].

However, isoconversional methods under dynamic conditions are widely used and recommended. The development and practical application of isoconversional methods were presented by Vyazovkin in his monograph [56].

KCE as the Arrhenius law

The typical Arrhenius plot of $\ln k_{iso}$ vs. $1/T_{iso}$ (Fig. 7) is also interesting. According to this plot, the value of the constant reaction rate increases $k_{iso} \uparrow$ with the increase in temperature $T_{iso} \uparrow$.

If we analyze the endothermic reaction of solid dissociation based on Eq. 8, then:

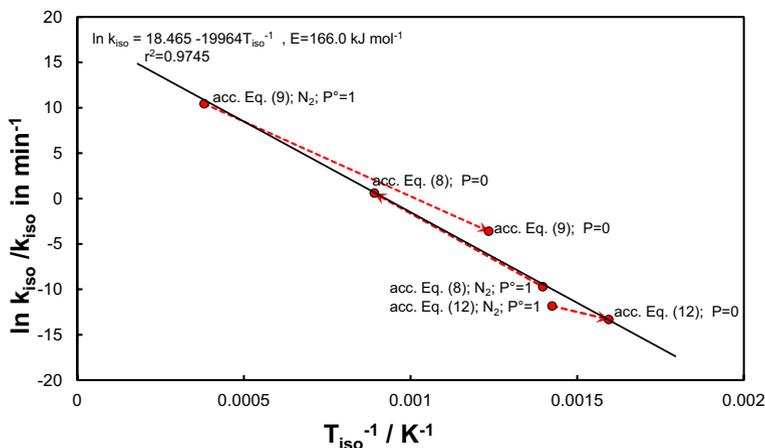


Fig. 7 Arrhenius plot for the estimators given in Figs. 3a, b and 4a, b, $P^o = 1$ atm (0.1 MPa) $P \sim 0$ MPa, numbers in brackets indicate the number of the equation, arrows indicate the direction: ← towards gas products, → towards substrates

1. the law is valid if the pressure is reduced $P \downarrow$ from atmospheric pressure to vacuum. It is logical from a thermodynamic point of view because the reaction becomes irreversible by removal of gaseous products, whereas when we use isoconversional methods of Eqs. 9 and 12, then:
2. the law is also correct when we consider increasing the pressure $P \uparrow$ from vacuum to atmospheric pressure. However, from a thermodynamic point of view for such reaction (endothermic dissociation of solids), this is illogical because in this case the increase in pressure directs the course of the reaction towards the substrates.

Distinguishing between pressure change directions with the same direction as the Arrhenius law is consistent with the assumptions presented in [55].

Concluding remarks

Determination of kinetic parameters based on the results of thermal studies using the most popular integral isoconversional methods, i.e., KAS and Vyazovkin, is still a currently studied topic [57]. Calculated activation energy values confirm its variability depending on the degree of conversion. In the case of analysis of the KCE or EEC [53, 58–62], correctness of kinetic parameter estimation ($\ln A$ and E) is verified by a parameter called the "compensation temperature". This temperature is defined by Krug [63] as "the temperature at which enthalpy variations precisely cancel entropy variations such that rate or equilibrium constants are completely invariant". Considering the conclusions presented in [55], we can assume that thermodynamic principles in the form of EEC related to temperature compensation are the source of KCE. In the case of isoconversional methods, $\ln A$ vs. E reveals weaker variability than we observe for isothermal and dynamic methods. The slight increase in $\ln A$ to E in the extreme case causes the slope in Eq. 2:

$$\text{if } \frac{1}{RT_{iso}} \rightarrow 0 \text{ then } T_{iso} \rightarrow \infty, \quad (23)$$

to tend to zero, and as a result, the compensation temperature reaches very high values (Fig. 4a). The differences in the variability of $\ln A$ to E are blurred for results obtained based on tests carried out in vacuum (Fig. 4b). Experiments in vacuum cause reactions to take place irreversibly, without reaching equilibrium and without thermodynamic limitations. Consequently, we observe relationships of $\ln A$ vs. E those determined by isoconversional and dynamic methods.

The methodology presented by Vyazovkin assumes a constant value of the pre-exponential factor $\ln A = \text{const}$. Consequently, according to Eq. 23 in the limiting case $T_{iso} \rightarrow \infty$, the compensation temperature is not determined, and it cannot be assigned its specific meaning, as in the case of KCE and EEC analysis.

Conclusions

1. The existence of at least two pathways for KCE resulting from the isochronal ($q = \text{const}$) and isoconversional ($g(\alpha_j) = \text{const}$) effects can be demonstrated under dynamic conditions. The combination of these two effects in the form of Eq. 10 indicates scattering of the KCE.
2. KCE for isoconversional methods is loosely related to EEC when at the isokinetic temperature $T_{iso} \rightarrow \infty$, because the KCE is not a compensating quantity in the literal sense. If the pairs of thermodynamic activation functions (ΔS^* , ΔH^*) were determined from pairs ($E, \ln A$), the compensation temperature, also known as isokinetic, may be related to the equilibrium temperature, or inversion temperature. In such cases, the KCE and EEC are interdependent, but retain their originality in their interpretation.
3. In the Arrhenius relationships analyzed, we found that the increase in temperature is accompanied by an increase in pressure from vacuum to atmospheric pressure, which is not thermodynamically justified for this type of reaction because in this case, the increase in pressure directs the course of the reaction towards the substrates.
4. Under isothermal conditions (but analyzed as polyisothermal) the only source of KCE in the form of isoconversional effects appears. Simultaneously, the polyisothermal system generates a latent function in the mathematical form Eq. 14. This process does not make physical sense but explains the source of dispersion, leading to systematic errors.
5. This method of analyzing from dynamic to (poly)isothermal conditions was deliberate, due to the demonstrated isochronal and isoconversional sources of KCE, which just depend on the method of analysis of data obtained in a specific assumed time–temperature field.
6. Barrie performed multivariate calculations regarding the KCE random experimental [27] and systematic errors [28]. These considerations can be supplemented by the ambiguity resulting from the use of the calculation of correlation (confidence ellipse) [38] and frequently observed deviation from the linear relationship in

Eq. 2, e.g., [39]. In this case, the isokinetic temperature does not have to be unambiguous and characteristic, because its difference can be even more than 100 K by approximation of the KCE slope in the relationship $(RT_{iso})^{-1} = \text{slope} \pm \text{deviation}$. Hence, the accuracy of experiments and kinetic models are probably less precise than expected.

- Using different methodologies (kinetic models) and computational techniques to develop sets of experimental data leads to different values of kinetic parameters. The resulting kinetic parameter sets are arranged in straight lines and practically coincide with the ellipses of 95% confidence (Fig. 5). The increase in activation energy is compensated by the increase in the pre-exponential factor and the inverse relationship is not possible [64].
- The isoconversional KCE may result from the adopted calculation methods and not from experimental data in situ, which results in variation of the activation energy.

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