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Isokinetic and Compensation Temperature in the Analysis of Thermal Dissociation of the Solid Phase under Dynamic Conditions

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Abstract: Sets of Arrhenius parameters, determined according to known different equations for dynamic conditions, in the vast majority form the Kinetic Compensation Effect (*KCE*). Converting these data to the simplified components of the Eyring equation comes down to Enthalpy–Entropy Compensation (*EEC*), which is consistent with the second law of thermodynamics. It has been proved that the impact of the generally known Coats−Redfern solution on the equation in differential form results in an isokinetic form of the equations and a very important coordinate $[T_0; \alpha_0]$ (initial temperature and conversion degree), depending on the heating rate. This makes it possible to determine the parameters of Arrhenius' law for both in silico and experimental data. An analytical method for determining this coordinate has been proposed. These considerations have given rise to an analysis of the relationship between two temperatures: initial and isokinetic. The sense of isokinetic temperature has been verified by the parameters *CQF* and *K*. Going further, it was found that the effects of *EEC* can be transformed into *KCE* and vice versa, which means that the two temperatures should be identical, i.e., $T_{iso} = T_c$. However, the experimental data indicate that the analyzed temperatures form a sequence $T_0 \leftrightarrow T_{iso} \leftrightarrow T_c \leq T_{eq}$, where T_{eq} is the equilibrium temperature.

Keywords: isokinetic and compensation temperature; isokinetics; kinetic compensation effect; enthalpy–entropy compensation

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1. Introduction

The compensation effects described in the literature occur during both kinetic and thermodynamic studies. In the case of kinetic studies, they are related to the Arrhenius law and are described by the Kinetic Compensation Effect (*KCE*). *KCE* is sometimes called the Iso-Kinetic Relation (IKR) [1] or less commonly IE (Isokinetic Effect) [2]. In thermodynamic analysis, compensation effects called *EEC* (Enthalpy Entropy Compensation) result from van't Hoff's law. Freed [3] lists 54 references relating to various possibilities of *EEC* occurrence. The common feature in both cases (for both types of compensation effects) is the occurrence of characteristic temperatures as constant values: isokinetic for *KCE* (T_{iso}) and compensation for *EEC* (T_c), respectively.

1.1. Outline of the Problem

Taking the most general course of consideration according to [4], the mentioned effects can be presented in the form of Equations (1)–(3) for $\beta, \gamma = \text{const}$:

$$\ln A_i = \gamma + \frac{E_i}{R\beta} \quad (1)$$

$$\Delta H_i^{+} = \gamma + \beta \Delta S_i^{+} \quad (2)$$

or

$$\Delta H_i^{\varnothing} = \gamma + \beta \Delta S_i^{\varnothing} \tag{3}$$

In Equations (1)–(3), the β symbol stands for T_{iso} (Equation (1)) and T_c (Equations (2) and (3)) suggesting that these are the same temperatures in a value sense. Provided between Equations (1) and (2) there are approximate, although reliable relationships, the reference of the same equations to thermodynamic standard functions is not obvious. The formal notation of Equation (3) has been demonstrated for many chemical, biochemical or physicochemical reactions/processes [1,4–9].

In the Gold Book [10] Equation (2) is presented as isokinetic relationship:

$$\Delta H_i^{+} - \beta \Delta S_i^{+} = \text{const} \tag{4}$$

and Equation (3) is related to chemical reaction as the isoequilibrium relationship:

$$\Delta_r H - \beta \Delta_r S = \text{const} \tag{5}$$

Equations (4) and (5) and also (1) express the view of Freed [3], who (briefly) postulates that the compensation or isokinetic temperature is determined by the identity of the chemical equilibrium constants or kinetic constants, respectively. In the first case, van't Hoff's isobar together with the Gibbs free energy is used in the proof and reduced to *EEC*, and the second is commonly known and accepted as *KCE*, and is related to the Arrhenius equation.

By way of theoretical considerations, Starikov proved the validity of Equation (3) based on Bayesian statistical mechanics [11]. Equations (2) and (4) contain thermodynamic activation functions derived from Eyring's theory from 1935 [12]. The theory has been adapted for modeling complex reaction/process pathways, as well as for the practical use of selected relationships captured by Equations (2)–(5) [1,3,5,8,9,13–20]. Some of the mentioned works combine Eyring's theory with the Arrhenius equation [13,14,18].

Analyzing the experimental data obtained under isothermal and dynamic conditions, a large discrepancy in the values of determined isokinetic temperatures can be observed. The application of isothermal, dynamic or isoconversional kinetic functions for modeling does not lead to one common isokinetic temperature value [20]. Thus, it can be expected that the reliability of Equation (2) or Equation (4) is dependent on the parameters determined from kinetic equations or reduced to thermokinetics, consistent with the classical Arrhenius equation, i.e., ln A vs. E. Consequently, the possibility of confronting the isoconversion and compensation temperature relationships arises.

In this type of analysis, temperatures defining the initial temperature [21] or [22] and isokinetic are still useful. The equilibrium temperature follows from Equation (5) when we introduce const = 0, i.e.,

$$T_{eq} = \frac{\Delta_r H^{\varnothing}}{\Delta_r S^{\varnothing}} \text{ when } \Delta_r G^{\varnothing} = 0 \tag{6}$$

In this work, an attempt is made to use the isokinetic (T_{iso}) and compensation (T_c) temperatures as quantities representative for considered kinetic functions $f(\alpha)$ to demonstrate isokinetics, which is largely understood as the closeness of the Arrhenius law parameter values determined by the known equations.

1.2. Aim of the Paper

Kinetic considerations provide an opportunity to assess isokinetic relationships based on general kinetic equations [23,24] and selected initial conditions that depend on the heating rate. This creates a temperature sequence in observing the progression of the reaction/process from an initial state to an irreversible state with respect to temperature under conditions of its linear increase $q > 0$:

$$T_0 = \text{var vs. } q; T_m = \text{var vs. } q; T_{iso},\ T_c \text{ and } T_{eq} = \text{const when } P = \text{const} \tag{7}$$

Temperatures with symbols T_0, T_m, T_{iso} are determined by kinetic experiments. Temperature T_c can be of both kinetic and thermodynamic meaning, while T_{eq} is only thermodynamic. The temperature T_m denotes the temperature of the maximum reaction/process rate characteristic for dynamic conditions.

The following equation is the starting point for the analysis of kinetics of processes/reactions tested under non-isothermal conditions, also called dynamic conditions:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{q} f(\alpha) e^{-\frac{E}{RT}} \tag{8}$$

Approximations in the form presented in the works [21,23,25–30] are most often used as solutions of Equation (8), while other known solutions will be omitted here.

In practice, the Coats−Redfern approximation is most commonly used in the form of a temperature integral (or, less commonly, an incomplete gamma function):

$$g(\alpha) = \frac{ART^2}{qE} e^{-\frac{E}{RT}}, \quad q = \mathrm{const} \tag{9}$$

Presenting the occurrence of the isokinetic temperature at low conversion degrees $(\alpha = 0.01 - 0.05)$ [21] will mean there is an initial state:

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{T_0} = \frac{1}{T_0} \tag{10}$$

The aim of this study is to determine from Equations (8)–(10) in what form we observe the isokinetic relationship of the selected models described symbolically as $f(\alpha)$ or $g(\alpha)$, in order to further analyze the variability of the temperature series presented in Equation (7) and the mutual relations between these temperatures.

2. Methods

2.1. General Kinetic Equation for Dynamic Conditions

If we introduce Equation (9) into Equation (8), we obtain the equation also found in the literature [27], and earlier in [28]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = f(\alpha) \cdot g(\alpha) \cdot \frac{E}{RT^2} \tag{11}$$

Presenting Equation (11) in form:

$$\int \frac{\mathrm{d}\alpha}{f(\alpha) \cdot g(\alpha)} = -\frac{E}{RT} + C \tag{12}$$

the integral on the left-hand side of the equation after substitution: $\mathrm{d}\alpha = f(\alpha) \cdot \mathrm{d}g(\alpha)$ leads to the form:

$$\ln[g(\alpha)] = -\frac{E}{RT} + C \tag{13}$$

Equation (13) satisfies the criteria of the mathematical formalism for different kinetic functions $g(\alpha)$–however, deviations from the assumed activation energy can be expected.

Table A1 uses the proposition from the book [31] having in mind explicitly given variables and coefficients depending on the definition of the function $f(\alpha)$. It can also be considered that these are the most common kinetic models. It should be noted that Table A1 (see: Appendix A) does not present all known functions–0th kinetics (R1) and higher orders, e.g., Johnson-Mehl-Avrami [27], D4 Ginstein-Brouhnstein [32], Dahme-Junker [33], or more complicated ones like Šesták-Berggren (SB) [32,34], are missing.

Thus, the intercept in Equations (12) and (13) can be represented as ($\ln[g(\alpha)]$ vs. $1/T$):

$$C = \ln[g(\alpha_0)] + \frac{E}{RT_0} \tag{14}$$

As in the work [23], the functions $g(\alpha)$ were replaced with sufficient accuracy by the first term of the expansions into a power series ($\ln[g(\alpha_0)]$ for small α_0 in Table A1).

The constant written in the form of Equation (14) contains the sought after two unknowns as the coordinate $[T_0;\alpha_0]$ at the initial point and requires a special solution, when the kinetic function is a priori unknown.

Expressions for the simplified constant C $\left(C = n\ln\left(\frac{\alpha_0}{m}\right) + \frac{E}{RT_0},\ n,\ m = \text{const}\right)$ are included in Table A1.

For arbitrary data, the combination of Equation (8) to Equation (10) was proposed for the coordinate $[T_0, \alpha_0]$ establishing the relation:

$$f(\alpha_0)\cdot g(\alpha_0) = \frac{RT_0}{E} \tag{15}$$

The integration constant in Equation (14) can be transformed into a complex form with the following components:

$$C = \ln[g(\alpha_0)] + \left[f(\alpha_0)\cdot g(\alpha_0)\right]^{-1} \tag{16}$$

The pre-exponential factor is determined from Equation (9) after reference to temperature $T = T_0$.

$$\ln A = \ln[g(\alpha_0)] + \frac{E}{RT_0} + \ln\left(\frac{qE}{RT_0^2}\right) \tag{17}$$

According to Equation (14) the first two terms to the right of Equation (17) are the integration constant, hence we obtain:

$$\ln A = C + \ln\left(\frac{qE}{RT_0^2}\right) \tag{18}$$

Equation (18) is valid for all kinetic models, including those for which $f(\alpha_0) \neq 1$, as can be shown by inserting the logarithmized Equation (9) into Equation (14) for $T = T_0$. In Equation (17) after rearranging the products under the logarithms (or substituting into Equation (18) the integration constant from Equation (14)) we obtain Equation (19):

$$\ln A = \ln\left[g(\alpha_0)\cdot\frac{E}{RT_0}\right] + \frac{E}{RT_0} + \ln\left(\frac{q}{T_0}\right) \tag{19}$$

and after using Equation (15) and performing operations we obtain:

$$\ln A = -\ln[f(\alpha_0)] + \frac{E}{RT_0} + \ln\left(\frac{q}{T_0}\right) \tag{20}$$

For the most commonly used models it can be assumed that for F1 $f(\alpha_0) \cong 1$ (for R1: $f(\alpha_0) = 1$, so Equation (15) takes the form:

$$g(\alpha_0) = \frac{RT_0}{E} \tag{21}$$

which for $f(\alpha_0) = 1$, $g(\alpha_0) = \alpha_0$ and so Equation (21) leads to the next form:

$$\alpha_0 = \frac{RT_0}{E} \tag{22}$$

After introducing Equation (17) into Equation (16), we obtain an expression containing only the unknown temperature T_0:

$$C = \frac{E}{RT_0} - \ln\left(\frac{E}{RT_0}\right) \tag{23}$$

In turn, introducing Equations (21) and (22) we obtain an expression containing only the unknown conversion degree α_0:

$$C = \frac{1}{\alpha_0} + \ln \alpha_0 \tag{24}$$

Knowing the intercept in the relationship $\ln[g(\alpha)]$ vs. $1/T$, the initial conversion degree can be determined from Equation (24). In Equation (20), the inversion of the coordinate system for $T = T_0$ and after double-sided logarithmizing leads to:

$$\ln\left(\frac{q}{T_0}\right) = \ln A + \ln[f(\alpha_0)] - \frac{E}{RT_0}, \ \frac{q}{T_0} = \text{var} \tag{25}$$

Such inversion is similar to the transformation of Equation (9) into the well-known *KAS* equation. For most kinetic models, the term $\ln[f(\alpha_0)]$ can be neglected, and if the analytical form of the kinetic function and α_0 is known, it is not a problem to determine this value. It directly affects the accuracy of the determination of $\ln A$.

2.2. Data Set for Verification of Kinetic Models

Two data sets were used in this study, the first resulting from the simulation of the assumed Arrhenius parameters and for Equation (9) and $g(\alpha) = \langle\alpha\rangle$, i.e., $E = 200$ kJ·mol^{-1}, $A = 10^{14}$s^{-1} and five heating rates $q = 0.01;\ 0.03;\ 0.1;\ 0.3;\ 0.5K{\cdot}s^{-1}$, respectively. The calculations were carried out for the temperature range $T = 298 - 1000$ K with a step $\Delta T = 1$ K, choosing the α values from the range $[0;\ 1]$, similarly to what was adopted in [21]. To distinguish the notation for individual cases of the function $g(\alpha)$ values, a single-column matrix is marked as:

$$g(\alpha) = \langle\alpha\rangle \text{ or } g(\alpha) = g\langle\alpha\rangle,\ \langle\alpha\rangle \in [0;1] \tag{26}$$

when $\langle\alpha\rangle$ is an invariant of the kinetic models.

The second set of experimental data was taken from the work [19], which was extensively analyzed in full by the ICTAC congress in 2000 [35]. They concern the dissociation of calcite in a nitrogen atmosphere, the most preferably proposed kinetic model being R1, F1 or fractional.

3. Results

3.1. Results of the Calculations

For kinetic models (Table A1) and exponents n for P4 (n =1/4), P3 (n =1/3), P2 (n = 1/2), P2/3 (n = 3/2), D1 (n = 2) and R1 (0th order, n = 1), the left-hand side of Equation (13) is as follows:

$$n\ln\langle\alpha\rangle = -\frac{E}{RT} + C \tag{27}$$

which reduces the listed models to 0th order kinetics.

Similarly for models F1 (n = 1), A4 (n = 1/4), A3 (n = 1/3), A2 ($n = \frac{1}{2}$):

$$n\ln[-\ln(1 - \langle\alpha\rangle)] = -\frac{E}{RT} + C \tag{28}$$

For models R2 or R3 ($n = 1$) we obtain, respectively:

$$\ln\left(1 - \sqrt{1 - \langle\alpha\rangle}\right) = -\frac{E}{RT} + C \tag{29}$$

or:

$$\ln\left(1 - \sqrt[3]{1 - \langle\alpha\rangle}\right) = -\frac{E}{RT} + C \tag{30}$$

For the popular D3 model:

$$g(\alpha) = \left[1 - \sqrt[3]{1 - \langle\alpha\rangle}\right]^2 \tag{31}$$

after logarithmizing Equation (31) it transforms into R3 (Equation (30)).

For the control test, the reference model Equation (27) for $n = 1$ and for the assumed conditions $(E,\ A,\ q)$, Figure 1. Table 1 shows the calculated activation energies, integration constants (intercept of linear equations), temperatures and the corresponding conversion degrees as $[T_0;\ \alpha_0]$.

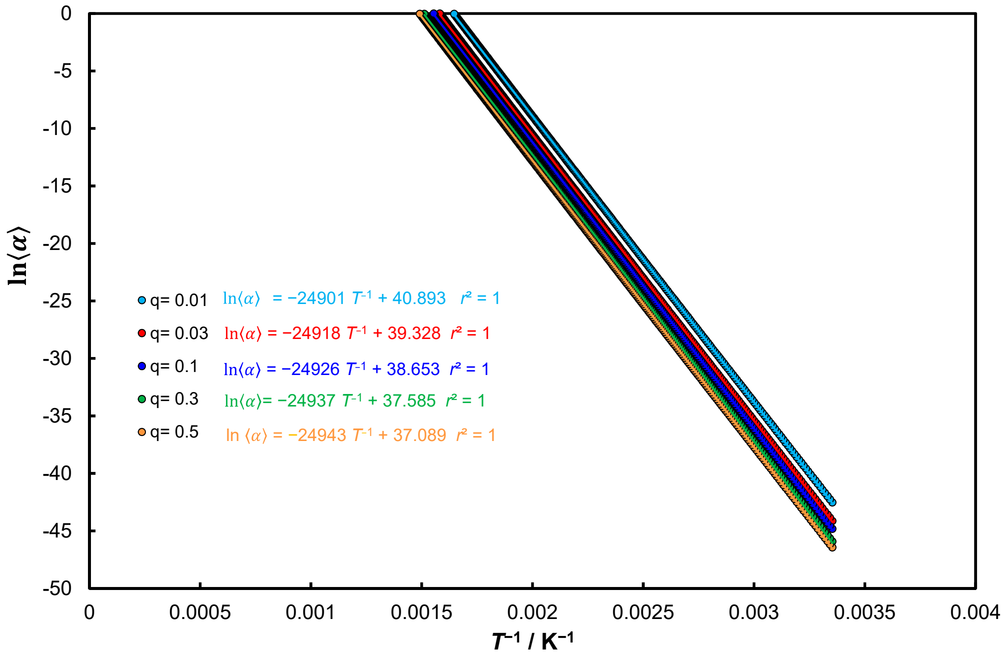

Figure 1. Kinetic approach Equation (27) for $n = 1$ for the assumed five heating rates.

Table 1. Summary of calculated parameters of Equation (27) for five assumed heating rates and $n = 1\left(r^2 = 1\right)$.

Heating Rate q**, K s**$^{-1}$	E**, kj mol**$^{-1}$ **acc. Equation (27)**	**Intercept C acc. Equation (27)**	T_0 **K from Equation (23)**	α_0 **from Equations (22) or (24)**	**ln**A **(**A **in s**$^{-1}$**) acc. Equation (18)**
0.01	207.03	40.890	557.2	0.02238	33.762
0.03	207.13	39.822	571.5	0.02294	33.738
0.1	207.23	38.651	587.9	0.02359	33.718
0.3	207.33	37.583	603.7	0.02422	33.686
0.5	207.38	37.087	611.4	0.02450	33.688
average ± standard deviation	207.22 ± 0.14	38.807 ± 1.569	586.3 ± 22.4	0.02353 ± 0.00088	33.718 ± 0.029

The numerical data summarized in Table 1 were verified using Equation (25). A graphical representation of the relationship obtained is presented in Figure 2. From the parameters of the obtained linear relationship:

$$\ln\left(\frac{q}{T_0}\right) = -\frac{23400}{T_0} + 32.144 \qquad \left(r^2 = 1.0000\right) \tag{32}$$

The activation energy $E = 199.53\ \text{kJ}\cdot\text{mol}^{-1}$ and the pre-expotential factor $A = 10^{13.966}\ s^{-1}$ were determined. As one can easily see, both determined parameters have slightly lower values than those used for calculations ($A = 10^{14}\ \text{s}^{-1},\ f(\alpha_0) = 1$).

The intercept value in Equation (32) is dependent on deviations of the activation energy and errors resulting from the observed variability of constants occurring in the kinetic functions.

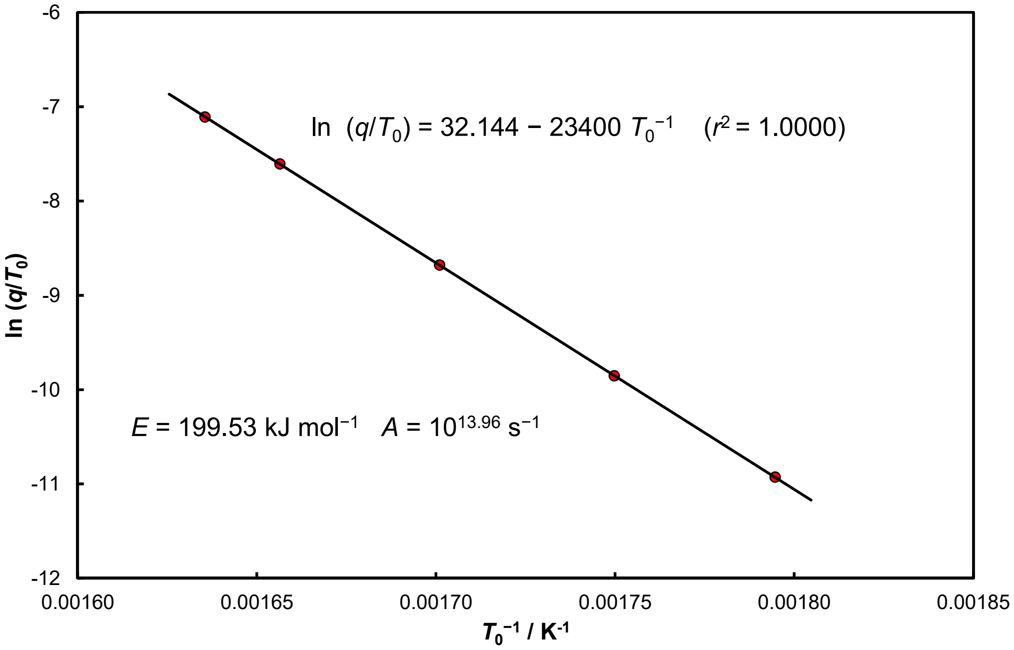

Figure 2. Data presented in Table 1 in the Equation (25) coordinate system.

Figure 3 presents the relationship (30) function D3 (Jander) but as R3: $\ln\left(1 - \sqrt[3]{1 - \langle\alpha\rangle}\right)$ (R3).

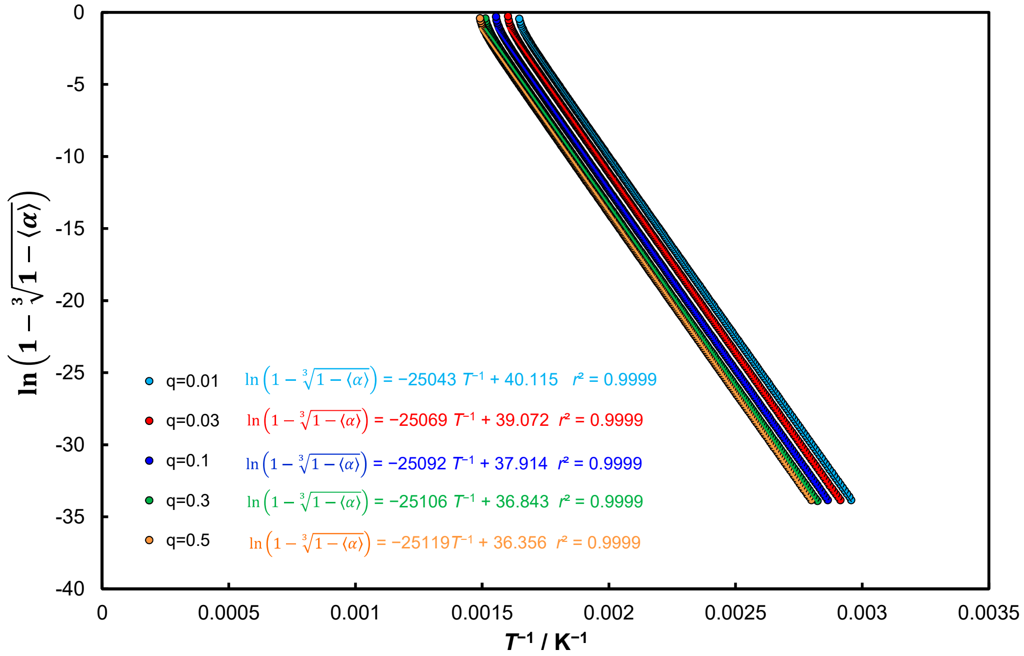

Figure 3. The relationship for function D3 (Jander) as Equation (30) for five different heating rates.

Table 2 gives as an example the integration constant calculated according to Equation (14), but also comparatively Equations (16), (23) and (24) were used–all the mentioned formulas turn out to be equivalent.

Table 2. Analysis of the kinetic function D3 as R3 by means of Equation (30), $r^2 = 0.9999$.

Heating Rate q**, K s**$^{-1}$	**Slope in Equation (30)**	**Intercept in Equation (30)**	E**, kJ mol**$^{-1}$	**Intercept acc. Equation (14)**	**ln**A **(**A **in s**$^{-1}$**) acc. Equation (20)**
0.01	25043	40.115	208.21	40.054 *	34.017
0.03	25069	39.072	208.42	38.999	34.010
0.1	25069	39.072	208.42	37.804	33.962
0.3	25106	36.843	208.73	36.776	33.980
0.5	25119	36.356	208.84	36.285	33.976
average ± standard deviation	-	38.29 ± 1.31	208.52 ± 0.23	37.984 ± 1.392	33.989 ± 0.021

* For $[T_0;\ \alpha_0]$ of Table 1 and slope in Equation (30).

Thus, if this model accepts the coordinates $[T_0;\ \alpha_0]$ then by force of facts Equation (25) remains unchanged in the analytical form of Equation (32).

Model D2 is very interesting because starting from infinitesimally small conversion degrees it goes from R1 through D1 to D2.

The consequences of the considerations for the assumed values of kinetic parameters $E = 200\ \text{kJ}\cdot\text{mol}^{-1}$ and $A = 10^{13.966}\ s^{-1}$ also provide an opportunity to analyze the isoconversion models.

The adopted methodology and the performed cycle of calculations indicate the possibility of extending the interpretation of Equation (9) it can be written in a form as *KAS* equation:

$$\ln\left(\frac{q}{T_i^2}\right) = -\frac{E}{RT_i} + \ln A - \ln\left(\frac{E\cdot g(\alpha_i)}{R}\right) \tag{33}$$

For each point with coordinates $[T_i;\ \alpha_i]$, an intercept is created: $\ln A - \ln\left(\frac{E\cdot g(\alpha_i)}{R}\right) = \text{const}$, and for the presented considerations the relationship $g(\alpha_i) = \alpha_i$ has been assumed, what follows from considerations on Equation (13) and further ones. Figure 4 and Table 3 summarize the results of calculations for five different heating rates and for constant values of the conversion degree α_i from 0.1 to 0.8.

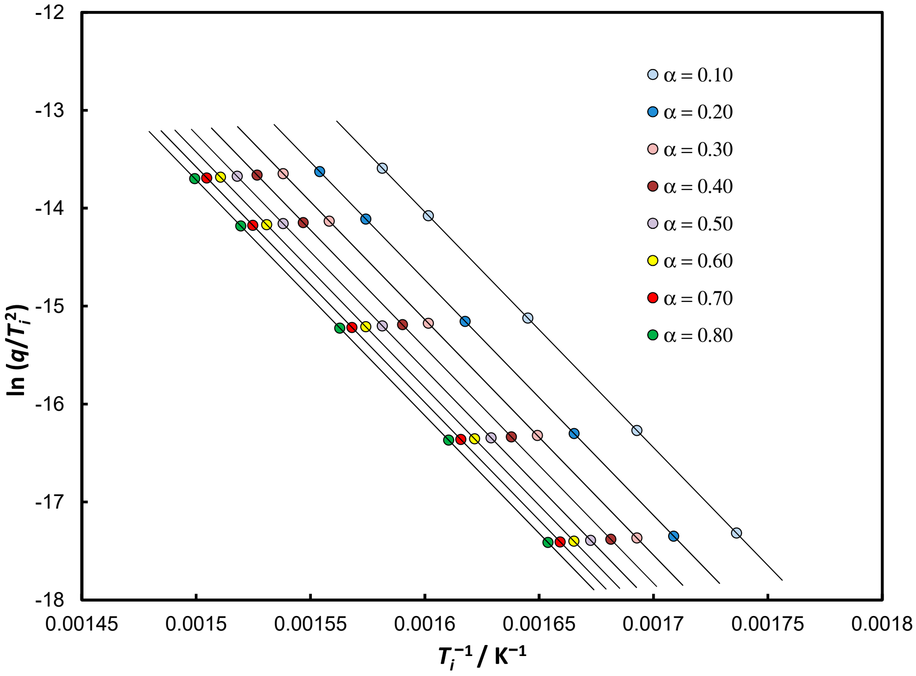

Figure 4. Analysis of the theoretical data Equation (33) for the assumed values of the parameters of the Arrhenius law in isoconversion approach for eight positions of α = const and five different heating rates.

Table 3. Summary of calculation results for five different heating rates and for constant values of the conversion degree α_0. $\log A = 14.00$ $\ln A = 32.236$ $r^2 = 1.0000$.

Conversion Degree, α_0	**$\frac{E}{R}$ in Equation (33)**	**Intercept in Equation (33)**	**ln*A* (*A* in s^{-1})**	***E*, kJ mol^{-1}**
0.1	24056	24.451	32.236	200.00
0.2	24052	24.451	32.231	199.97
0.3	24053	23.347	32.231	199.97
0.4	24054	23.062	32.234	199.99
0.5	24055	22.840	32.235	199.99
0.6	24062	22.668	32.246	200.05
0.7	24055	22.504	32.235	199.99
0.8	24055	22.371	32.236	200.00
average ± standard deviation	-	-	32.236 ± 0.004	200.00 ± 0.02

The data presented in Table 3 show that with the relative error below 0.02% we determine the activation energy E and with a similar approximation, the pre-exponential factor A. Despite the very small differences in values, we can derive *KCE* as an isoconversional effect $(\alpha = \text{const})$:

$$\ln A = 0.1864E - 5.0363,\ E \text{ in kJ mol}^{-1},\ T_{iso} = 645.27\text{ K}\left(r^2 = 0.9923,\ sl = 0.0(6)\right) \quad (34)$$

The determined isokinetic temperature is higher than that provided in Table 1 even for heating rate $q = 0.5\text{ K}\cdot\text{s}^{-1}$, but more important is the fact that there appears a *KCE* that is statistically significant only for the isoconversion method.

The starting point of the calculation is the integration constant Equation (13), which initiates the possibility of confronting Equation (25), since formally in both cases $E = \text{const}$. Considerations for simulated data show that the integration constant (C) in Equations (14), (16), (19), (20) divides the kinetic data into a range of very low reaction/process rates from those corresponding to the higher temperature range and heating rates $\frac{d\alpha}{d\ln T} > 1$.

The *KCE* phenomenon, conventionally written as Equation (1) for $\beta = T_{iso}$ is characterized by the fact that $\frac{d\ln A}{dE} = \left(RT_{iso}\right)^{-1} = \text{const}$, so there is no simple way to relate to Equation (25) due to the variability of the ratio $\frac{q}{T_0} = \text{var}$ for $E = \text{const}$. Note that even in the simplest kinetic case for the simulated R1 model this effect does not occur (Table 1). This fact is also confirmed by the data for model R3 (Table 2). A small increase in E leads to a small decrease in $\ln A$, which contradicts the classical Arrhenius law [2], but is possible for physical processes. An example is the relationship between the two parameters of viscosity in the Arrhenius-like equation, such as the energy and the pre-exponential factor; see Figure 3b in [36].

At this stage of consideration, the importance of the initial temperature (T_0) is confirmed, but there is not enough strong evidence to consider the isokinetic temperature (T_{iso}) as an undisputed quantity. From the data considered, it appears that $T_{iso} > T_0$.

3.2. Thermokinetic Analysis of Experimental Data

The starting point for kinetic considerations is Equation (13) and the assumption that $g(\alpha) = \alpha$ (e.g., Anderson in [35]). This is supported by Equation (33) as well as the calculations presented in Table 4, although it will be necessary to verify this assumption. The calculations were based on the experimental data presented in [19] (Table 1a in [19]) for thermal dissociation of calcite in nitrogen under dynamic conditions.

Bearing in mind the need to determine E and $\ln A$, it was found that there are at least two possibilities to analyze the experimental data. The first option is to use the relationship:

$$\ln\left(\frac{\alpha}{T^2}\right) = \ln\left(\frac{A\cdot R}{q\cdot E}\right) - \frac{E}{R\cdot T},\ q = \text{const} \quad (35)$$

while the second one uses the Doyle approximation for the intercept presented in [20]:

$$\ln\alpha = \ln\left(\frac{0.005\cdot A\cdot E}{q\cdot R}\right) - \frac{E}{R\cdot T},\ q = \text{const} \tag{36}$$

Table 4. Analysis of experimental data of thermal dissociation of calcite in nitrogen based on Equation (36)–Doyle approximation.

Heading Rate, *q*, K·(60s)$^{-1}$	**$\frac{E}{R}$ in Equation (36)**	**Intercept in Equation (36)**	**r^2**	**E, kJ·mol^{-1}**	**ln*A* (*A* in s^{-1})**	**T_0, K acc. Equation (23)**
1	24,576	24.712	0.9994	204.32	15.81	876.3
3	24,651	23.798	0.9986	204.95	15.99	909.7
5	24,222	22.849	0.9988	201.38	15.57	927.6
7.5	24,612	22.837	0.9991	204.62	15.94	943.0
10	24,565	22.484	0.9992	204.23	15.88	954.6
15	24,685	22.176	0.9997	205.23	15.97	971.4
25	24,836	21.850	0.9997	206.49	16.15	990.6
average ± standard deviation	-	-		204.46 ± 1.44	15.90 ± 0.17	939.0 ± 35.6

Equations (35) and (36) can be applied to isoconversional analyses in the form:

$$\ln\left(\frac{q}{T_0^2}\right) = \ln\left(\frac{A\cdot R}{E\cdot\alpha_0}\right) - \frac{E}{R\cdot T_0},\ \alpha_0 = \text{const} \tag{37}$$

when Equation (37) is a special case of Equation (33) and Equation (38):

$$\ln q = \ln\left(\frac{0.005\cdot A\cdot E}{R\cdot\alpha_0}\right) - \frac{E}{R\cdot T_0},\ \alpha_0 = \text{const} \tag{38}$$

Experimental data of the thermal dissociation of calcite in nitrogen for the seven heating rates in the coordinate system of Equation (35) are presented in Figure 5.

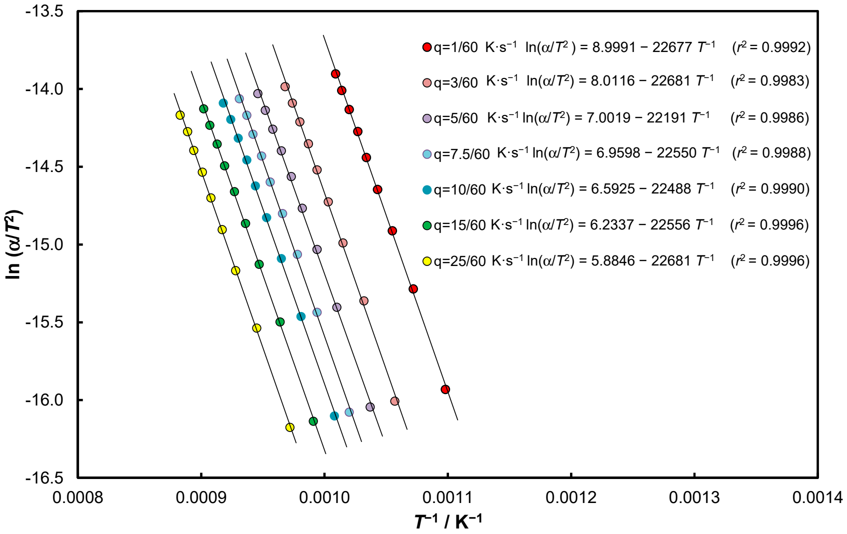

Figure 5. Experimental data of thermal dissociation of calcite in nitrogen for seven heating rates and nines positions of α = const. in the coordinate system of Equation (35).

Equations (35)–(38) generate *KCE* and therefore the individual estimators were statistically verified–all relationships are significant with a probability of at least 99.99%. The relevant graphs are shown in Appendix A in Figures A1–A4, while whether the determined isokinetic temperatures can be considered authoritative will be presented later in the paper.

Equation (36) can be taken as analogous to Equation (13) for $g(\alpha) = \alpha$, by which, using Equation (19), the initial temperature T_0 can be determined. The obtained data were collected in Table 4, resulting in a confrontation similar to Equation (25)—Figure 6; this is a methodological comparison to Figure 2.

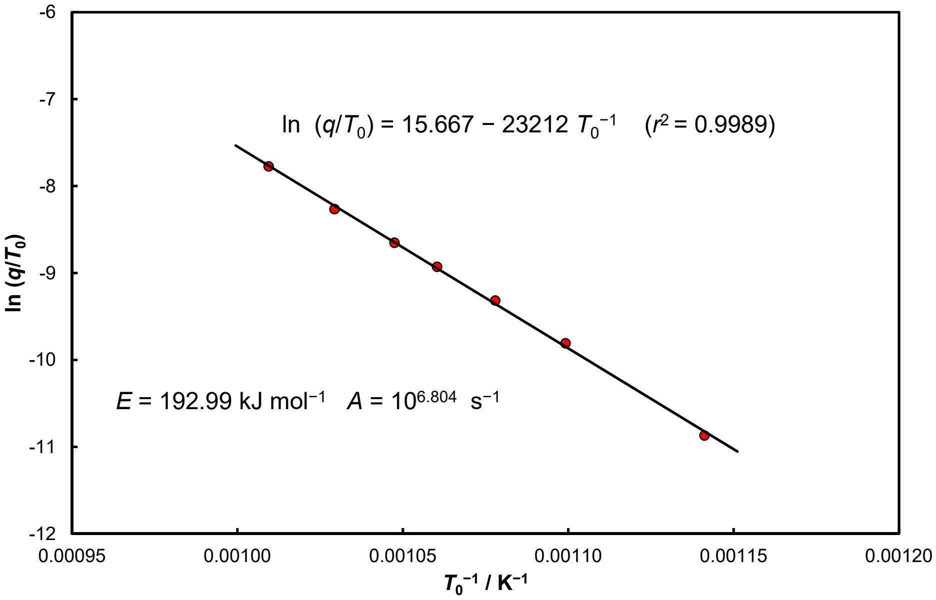

Figure 6. Experimental data of the thermal decomposition of $CaCO_3$ in nitrogen for seven heating rates in the coordinate system of Equation (25).

Based on the data summarized in Table 4, the following form of Equation (25) was determined:

$$\ln\left(\frac{q}{T_0}\right) = -\frac{23212}{T_0} + 15.6671 \quad \left(r^2 = 0.9989\right) \tag{39}$$

from which $E = 192.99$ kJ·mol^{-1} and $A = 10^{6.80}\ s^{-1}(\ln A = 15.67)$ were calculated assuming $f(\alpha_{iso}) = 1$ (Figure 6).

The data from Table 4 $[q;\ T_0]$, as presented in Figure 6, confirm sufficient agreement with the data presented in the descriptions of Figures A1–A4, in particular, the value of both the activation energy and the frequency constant are close to the values given in the description of Figure A2. Obviously, the average values given in Table 4 $[\ln A;\ E]$ are identical to those given in Figure A3a.

Continuing the discussion, it should be stated that the experimental data analyzed with Equation (36) are interpreted twice. Originally, according to Equation (36), the intercept being a Doyle approximation allows us to determine the frequency constant A and the slope (the activation energy E). Hence, one obtains the *KCE* relation and further the isokinetic temperature T_{iso}. On the other hand, the intercept was interpreted according to Equation (19) by iteratively determining T_0 for each heating rate (Table 4).

Analytical determination of the coordinate $[T_0;\ \alpha_0]$ for any kinetic data is complicated.

An interesting approach to the problem of determining this values $[T_0;\ \alpha_0]$ is the use of a three-parameter equation [19,23,27,37]. Equation (40) allows a different approach than that proposed in the paper [38]:

$$\ln\alpha = A_0 - \frac{A_1}{T} - A_2 \ln T \tag{40}$$

after differentiation of Equation (40) relative to temperature, for $T = T_0$ and introducing Equation (10) we obtain:

$$\frac{1}{T_0} = \alpha_0\left(\frac{A_1}{T_0^2} - \frac{A_2}{T_0}\right) \tag{41}$$

and after multiplying both sides by T_0^2 and after ordering, we get:

$$T_0 = \frac{\alpha_0 \cdot A_1}{1 + \alpha_0 \cdot A_2} \tag{42}$$

The approximate methods can be used to determine the coordinates $[T_0;\ \alpha_0]$ from the system of Equations (40) and (42).

After introducing Equations (42)–(40) for $T = T_0$ we obtain:

$$\frac{1}{\alpha_0} + \ln \alpha_0 + A_2 \ln\left(\frac{\alpha_0 A_1}{1 + \alpha_0 A_2}\right) = A_0 - A_2, \quad A_2 \neq 0 \tag{43}$$

This way we can skip the tedious analytical determination of higher order derivatives referred to in [38] in order to calculate T_0.

Table 5 summarizes the results of the experimental data analysis of the thermal decomposition of $CaCO_3$ in nitrogen for seven heating rates using the three-parameter Equation (40). The initial temperature T_0 was determined by an iterative method using the system of Equations (40) and (42), which omits the complicated search for this temperature discussed in works [21,22,38].

Table 5. Results of the analysis of experimental data on the thermal decomposition of $CaCO_3$ in nitrogen for seven heating rates using the three-parameter Equation (40).

Heating Rate q, K·(60s)$^{-1}$	A_0	**$A_1 \cdot 10^{-5}$, K**	A_2	**r^2**	**α_0 acc. Equation (43)**	**T_0, K acc. Equation (42)**	**$T_{\alpha=0.05}$, K [5]**
1	893.70	1.302	110.52	0.9993	0.0266	879.05	894.95
3	552.88	0.911	66.97	0.9999	0.0303	911.24	925.14
5	530.03	0.889	64.05	1.0000	0.0315	928.01	942.14
7.5	405.68	0.741	48.25	0.9999	0.0330	943.31	956.64
10	463.43	0.824	55.46	0.9999	0.0325	955.59	969.13
15	278.84	0.587	32.23	1.0000	0.0354	970.59	983.63
25	366.81	0.717	43.17	0.9999	0.0343	991.37	1004.62
average ± standard deviation					0.0319 ± 0.0027	939.88 ± 34.88	

From the data presented in Table 5 it can be seen that with increasing heating rate the value of isokinetic temperature increases. According to the notation of Equations (10) and (42), it can be concluded that, with an increase in the heating rate, the reaction rate decreases monotonically. For the heating rates analyzed in this paper, the variation of the isokinetic temperature was less than 4% hence, all the data can be taken as one average value.

The comparison of the initial temperatures provided in Tables 4 and 5 is surprisingly consistent, despite their determination on two independent paths.

3.3. Consequences of the Analysis of Experimental Data

It should be noted that the relations $\ln \alpha$ vs. $\frac{1}{T}$ are known in the literature as the temperature criterion [39] and are also discussed in works [40,41]. Equations (40) with (42), (43) are new elements in this respect and allow the determination of the isokinetic temperature.

As is known, the temperature criterion is valid for low conversion degrees. In the meantime, in this work, both in the part concerning model analyses (Figure 1) and experimental data of the thermal dissociation of calcite (Table 4), a linear relationship was obtained for all data, i.e., for the analyzed range of variation of conversion degree: as well for total range, as with its limitation, respectively.

While for model considerations this is acceptable, then for other more complicated solid decompositions after an initial stage with a high activation energy its value decreases with the conversion degree. The observations provided in [31] show that, in practice, different kinds of dependences of E on α can occur $(E = E(\alpha))$. On the other hand, in

Equations (35)–(38) with assumed Arrhenius parameters, the 0th order kinetics, $g(\alpha) = \alpha$ was used.

Nevertheless, what distinguishes this work from previous considerations is the possible range of variation of $\alpha \in [0.05; 0.9]$ to be analyzed, which omits the extremely important initial range for low conversion degree, as well as the end of the process. The first remark that comes to mind for comparison is the value of initial temperature–for the model it is equal to average $T_0 = 586.3$ K, while for the experimental data (Figures A1–A4) it depends on the adopted kinetic function and, see Table 4, on average it is equal to $T_0 = 939.0$ K (depending on q). When the experimental data for $q = \text{const}$ are analyzed using Equations (35) and (36), then $T_{iso} = 950 - 1061$ K. On the other hand, when we use isoconversion methods $(\alpha = \text{const})$ using Equations (37) and (38), we observe a wider range of variation $T_{iso} = 1074 - 1298$ K, which authorizes the conclusion that isoconversion methods are characterized by a much weaker increase in the $\ln A$ factor in relation to activation energy.

It should be noted that the parameters of the Arrhenius equation determined in this work from experimental data of the thermal decomposition of $CaCO_3$ in nitrogen have similar values and are in agreement with the data collected in [35] (e.g., Anderson): $E = 191$ kJ·mol^{-1}, $\ln A = 15.4/\ A \text{in}\ s^{-1}$.

For the four cases resulting from Equations (35)–(38), the determined Arrhenius law parameters can be treated as average values, as evidenced by the very small standard deviations. Nevertheless, these small variations generate an observable *KCE*.

Comparing the results of the analysis of the model and experimental data, it is clear that, in both cases, the values of the activation energies are similar, however, the frequency constant calculated for the experimental data reaches a much lower value: $A = 10^{6.80}\ s^{-1}(\ln A = 15.67)$, which makes the determined isokinetic temperatures take much higher values.

The kinetic Equations (35–38) were derived according to the presented model considerations, taking into account that the most important functional factor is the expression $\left(-\frac{E}{RT}\right)$. However, since in order to create the single column matrix (26) the relation (9) was used, in the derived equations also the occurring variable T^2 had to be taken into account. Therefore, it can be assumed that going from Equations (35) and (36) this variable weaves into the free expression and only slightly changes the values of the estimators, remaining in accordance with *KCE*, i.e., the values of estimators $\ln A$ and E increase or decrease simultaneously.

4. Discussion

4.1. Isokinetics and Initial Temperature

Accepting the general thermokinetic Equation (11), it was proved that the great majority of kinetic equations can be generalized to a single relationship (13), which contains the most important component $\left(-\frac{E}{RT}\right)$. Using the relationship (13) and forming the one-column matrix according to (26) one obtains a very practical for analysis of experimental data, Equations (27)–(31) with the intercept Equations (16), (19), (20), allowing us to determine the Arrhenius equation parameters and the initial (Equations (17) and (19)) or isokinetic temperature (Equation (1)).

We have complete agreement, when for the kinetic models presented in Table A1 the n factors provided there will be used as proposed in [23,24]. Using Equation (25) and the single-column matrix $\langle\alpha\rangle$ we obtain the basis for inferring the substitutability of kinetic functions of thermal dissociation processes of the solid phase. By forming the single-column matrix for the assumed Arrhenius law parameters, we can reproduce these parameters using a modification of Equation (25), e.g., in the form of Equation (34)–Table 3. The situation is even more favorable for experimental data, which are illustrated in Figure 6.

Despite the observed variation of the initial temperature values T_0 with heating rate during analysis of both model and experimental data (Tables 2, 4 and 5), the averaged values of E and $\ln A$ can be taken as correct. For these reasons, Equations (13) and (19), from which we determine the activation energy and the initial temperature, become significantly important.

In the case of experimental studies there is a possibility that Equations (13) and (19) will be valid in the whole experimentally determined range of conversion degree increase or in its selected range.

With the heating rate, the initial temperature T_0 increases, but the changing parameters of the Arrhenius law lead to a constant isokinetic temperature, $T_{iso} = \text{const}$.

The general forms of the Equation (13) can be reduced to the practical notation of Equation (24), which clearly indicates an extremely important element in thermogravimetric analysis for dynamic conditions, which is T_0. Its determination is much more convenient and simpler, when we use the three-parameter Equation (40) along with Equations (42) and (43).

4.2. Isokinetic Temperature

As demonstrated by Lente in his book [42], the problem of determining kinetic parameters can lead to incorrect or unjustified quantities. Generally, justified considerations on the correctness of the determined parameters of the Arrhenius equation may undoubtedly include another element connected with it–the isokinetic temperature T_{iso} or compensation temperature T_c, to which many works have been devoted, among others [4,21,41–47].

The temperature T_{iso} is determined by both Equation (1) and the classical *KCE* equation in the form, where intercept is expressed by the Arrhenius law, which formally makes it a tautology:

$$\ln A = \frac{E}{RT_{iso}} + \ln(k_{iso}) \tag{44}$$

where:

$$k_{iso} = A \cdot e^{-\frac{E}{RT_{iso}}} = \text{const} \tag{45}$$

When, in Equation (45), for each coordinate pair $[E; \ln A]$, the determined $T_{iso} = \text{const}$ leads to $k_{iso} = \text{const}$, then this is the "true" isokinetic temperature. The *KCE* in terms of (44) with (45) exhibits features of self-consistent equations. As will be shown further on, the fluctuation of the constant is relatively high despite $r^2 > 0.99$.

Thus, it can be considered that this leads to a *KCE* called horizontal (isoconversional). According to the analyses presented in [43–46], the isoconversional *KCE*, characteristic of isoconversional methods, can be described as the statistical compensation effect [45] characterized by high isokinetic temperatures.

The fundamental problem, however, is whether the general notation of *KCE* (Equation (1)), and specifically in the form of Equation (34) and in Figures A1–A4, makes physicochemical sense for a significant statistical level, as defined by high value of determination coefficient.

For this purpose, two criteria: *CQF* (Compensation Quality Factor) and K according to [48,49] were used. The analytical distinction in the *KCE* (and *EEC*) relations in both physicochemical and statistical sense for high determination coefficients $\left(r^2\right)$ for a specific number of N measurements was proposed. The K parameter can be called the position parameter.

For *KCE* assessment it is proposed:

$$CQF = 1 - \sqrt{\frac{1 - r^2}{\frac{1}{r^2}\left(\frac{T_{iso}}{T^*}\right)^2 - 2\left(\frac{T_{iso}}{T^*}\right) + 1}},\ 0 \le CQF \le 1 \tag{46}$$

$$K = 2\frac{\frac{1}{T_{hm}} - \frac{1}{T_{min}}}{\frac{1}{T_{low}} - \frac{1}{T_{high}}},\ \ T_{min} = \frac{T_{iso}}{r^2} \tag{47}$$

For a probability of 99% [48]:

$$CQF_{99} = 0.29 + \frac{1.41}{N^{0.57}} \tag{48}$$

The meaning of the symbols and more methodological and interpretive details are included in Appendix A.

Starting from the evaluation of the veracity of the determined isokinetic temperature in Equation (34), an important issue is the determination of the temperature designated as T_{low}. On the one hand, according to the data presented in Table 1, this is the average initial temperature $(T_{low} = 586.3\text{ K})$, but simulation analyses were carried out starting from a temperature of 298 K. The average temperature for $\alpha = 1$ was taken as the T_{high} temperature, i.e., $T_{high} = 643.2$ K.

For the first case using Equation (46) we get: $CQF = 0.37$ for $N = 8$ and according to Equation (48) $CQF_{99} = 0.721$ and Equation (47) $K = 1.22$, that is, the isokinetic temperature does not meet the criterion Equation (48). On the other hand, for the second version of $T_{low} = 298$ K we similarly obtain: $CQF = 925$ K; $K = 1.019$ and accept the physicochemical sense of the isokinetic temperature.

In this paper, the position parameter according to Equation (47) can be transformed to the form:

$$K = \left(1 - \frac{T_{hm}}{T_{iso}} r^2\right) \cdot \frac{T_{high} + T_{low}}{T_{high} - T_{low}} \tag{49}$$

which makes it possible to carry out a position analysis according to the characters in the expression shown in brackets, i.e., $\left(1 - \frac{T_{hm}}{T_{iso}} r^2\right) \le or \ge 0$, and $K \le 0\ or\ K \ge 0$. The favourable case can be defined as the inequality: $T_{hm} > T_{iso}$ when $r^2 = 1$, because $T_{iso} \to T_{low}$, which means approaching to the initial temperature T_o. When $T_{hm} \ll T_{iso}$, then this condition [43] characterizes isoconversional methods $(\alpha = \text{const})$ relative to classical methods $(q = \text{const})$.

For simplicity, still assuming $r^2 = 1$, this position parameter informs us about the relation between the isokinetic temperature and the range of tested temperatures in which it was determined, that is (Figure A5):

(a) $K = 0;\ T_{iso} = T_{hm};$
(b) $K < 0 (K = -1);\ T_{iso} < T_{low} (T_{iso} = T_{low});$
(c) $K > 0 (K = +1);\ T_{iso} > T_{high} \left(T_{iso} = T_{high}\right).$

Case (c) can lead to excessively high isokinetic temperatures.

Returning to the calculations presented in Figures A1–A4, it can be noted that, despite statistically satisfactory significance levels, none of the items meet the *CQF* criteria. Thus, the isokinetic temperatures are experimentally determined quantities that do not satisfy the *CQF* in the physicochemical sense.

These considerations indicate that an important issue is the temperature range in which we observe *KCE*, and it is advantageous that it is as wide as possible. Due to the "quality" of *KCE*, when $T_{hm} > T_{iso}$, then T_{iso} is closer to T_0 than to the final temperature of the reaction/process, which is relatively unfavorably much larger.

The criteria proposed in the works [48,49] may make it necessary to revisit many already published works.

4.3. Compensation Temperature

Eyring has derived an equation describing the reaction rate constant as a function of temperature and the free enthalpy of activation $\Delta G^{+} (p = p^{\varnothing} = 0.1\text{MPa})$ depending on the reaction mechanism limited by the formation of the active complex $\text{A} + \text{B} \to \left(\text{AB}\right)^{+}$ in gaseous phase [12]. The theses proposed in work [12] were adapted into the form of relations, in which the transmission coefficient and threshold energy distribution functions of the reactants were omitted [16,50–54] and only the "universal frequency term" $\frac{k_B T}{h}$ was left [51]. This expression is directly proportional to the product of $(R \cdot T)$ half equal to potential and kinetic energy [16]. The equation in its most common form is as follows:

$$k_{TST} = BTe^{-\frac{\Delta G^{+}}{RT}},\ B = \frac{k_B}{h} = 2.08364 \cdot 10^{10} (\mathrm{K} \cdot \mathrm{s})^{-1} \tag{50}$$

where:

$$\Delta G^{+} = \Delta H^{+} - T\Delta S^{+} \tag{51}$$

For the solid phase dissociation process following the reaction scheme: $\mathrm{A}^{(\mathrm{s})} \rightarrow \mathrm{B}^{(\mathrm{s})} + \mathrm{C}^{(\mathrm{g})}$ or $\mathrm{A}^{(\mathrm{s})} \rightarrow \mathrm{C}^{(\mathrm{g})}$ and the value of the stoichiometric coefficient for the substrate $\mathrm{A}^{(\mathrm{s})}$ $(\nu_A = 1, \sum \nu^{+} = 1 - \nu_A = 0)$ the equation is known in the form of Equations (50) and (51) [53]. The use of the presented approach seems to be common for thermal dissociation of the solid phase, such as for the complete decomposition of calcium oxalate ($\mathrm{CaC_2O_4 \cdot H_2O}$) to CaO [16].

Using the concepts of a certain convergence between the Arrhenius (k) and Eyring (k_{TST}) equations, from the equation $\frac{\mathrm{d} \ln k}{\mathrm{d}T} = \frac{\mathrm{d} \ln k_{TST}}{\mathrm{d}T}$ we obtain:

$$\Delta H^{+} = E - RT \tag{52}$$

while from the direct comparison of the constant rates $(k = k_{TST})$ we obtain:

$$\Delta G^{+} = E - RT \ln \frac{A}{BT} \tag{53}$$

Therefore, from Equation (51) and Equations (52) and (53) we determine the entropy of activation:

$$\Delta S^{+} = R\left[\ln\left(\frac{A}{BT}\right) - 1\right] \tag{54}$$

However, it should be noted that, despite the widespread acceptance of the presented comparison, there are premises which do not accept the concept of using the same set of input data [52].

On this basis, relationships between both activation thermodynamics and kinetics (parameters of the Arrhenius equation) are derived by taking the temperature of the maximum reaction rate as the activation temperature for dynamic conditions [53,54]:

$$\Delta H^{+} = E - RT_m \tag{55}$$

$$\Delta S^{+} = R\left[\ln\left(\frac{A}{BT_m}\right) - 1\right] \tag{56}$$

Suppose that Equations (55) and (56) satisfy the *EEC*, with a slope called the compensation temperature T_c (see Equation (2)), which directly follows from the second law of thermodynamics:

$$\Delta H^{+} = T_c \Delta S^{+} + H \tag{57}$$

or:

$$H = \Delta H^{+} - T_c \Delta S^{+} = \Delta G^{+}(T_c) = \mathrm{const} \tag{58}$$

By substituting Equations (55) and (56) into the form (57) and dividing the sides by $(R \cdot T_C)$, after transformation we get:

$$\frac{E}{RT_c} = \ln A - \ln(BT_c) + \frac{H}{RT_c} - \ln\left(\frac{T_m}{T_c}\right) + \frac{T_m}{T_c} - 1 \tag{59}$$

The sum of the last three components of Equation (59) is close to 0, which is evident either for $T_m = T_c$ or by taking the approximation: $\ln\left(\frac{T_m}{T_c}\right) \cong \frac{T_m}{T_c} - 1$. The derivation is also valid by taking $T = T_m$, so it shows features of generality, and Equation (59) takes the form *KCE*:

$$\ln A = \frac{E}{RT_c} + \ln(BT_c) - \frac{H}{RT_c} \tag{60}$$

The intercept in Equation (60) is:

$$\ln k(T_c) = \ln(BT_c) - \frac{H}{RT_c} = \text{const} \tag{61}$$

and is the logarithmic form of Equation (50) containing the *EEC* expressed by Equation (58).

Ultimately, Equation (60) takes the typical form for *KCE*:

$$\ln A = \frac{E}{RT_c} + \ln k(T_c) \tag{62}$$

which means the identity of the isokinetic and compensating temperatures, $T_{iso} = T_c$. The reverse possibility of transition from *KCE* (Equations (44) or (1)) to *EEC* (Equations (57) or (2)) can also be demonstrated.

From Equations (52) and (54) we extract the relevant Arrhenius parameters from the activation function at temperature $T = T_{iso}$:

$$E = \Delta H^+ + RT_{iso} \tag{63}$$

$$\ln A = \frac{\Delta S^+}{R} + \ln(BT_{iso}) + 1 \tag{64}$$

and after inserting Equations (63) and (64) into the *KCE* structure we obtain:

$$\Delta H^+ = T_{iso}\Delta S^+ + RT_{iso}\ln\left(\frac{BT_{iso}}{k_{iso}}\right) \tag{65}$$

Equation (65) satisfies the *EEC* expression of Equations (57) and (58). In addition, by substituting Equation (65) in the intercept: $T_{iso} = T_c$ and using the Arrhenius equation for $k_{iso} = k_c$, we again obtain Equation (53).

The treatment of the presented considerations is a continuation of papers [1,4,5,20] and is based on the relationship between the parameters of the Arrhenius law and Eyring's theory, from which it follows that the isokinetic temperature is equal to the compensation temperature. However, in the light of propositions to verify the physicochemical sense of the first mentioned [48,49] and one presented in Figures A1–A4 (see Appendix A), the determined quantities are reliable only from the point of view of statistical evaluation.

4.4. Isokinetic Temperature Again

In order to clarify the methodology of the experimental determination of isokinetic temperature, the parameters of the Arrhenius equation were used.

For the assumptions: $f(\alpha_0) = 1$, $g(\alpha_0) = \alpha_0$, Equation (22) determines the activation energy:

$$E = R\frac{T_0}{\alpha_0} \tag{66}$$

and using both Equation (19) and Equation (66) we obtain:

$$\ln A = \frac{1}{\alpha_0} + \ln\left(\frac{q}{T_0}\right) \tag{67}$$

The data illustrated in Figure A1 $(N = 7)$ and according to Equations (66) and (67) $(N = 7)$ were combined with an additional coordinate considered in this work as a reference in [35] (e.g., Anderson) $(N = 15)$ and are presented in Figure 7.

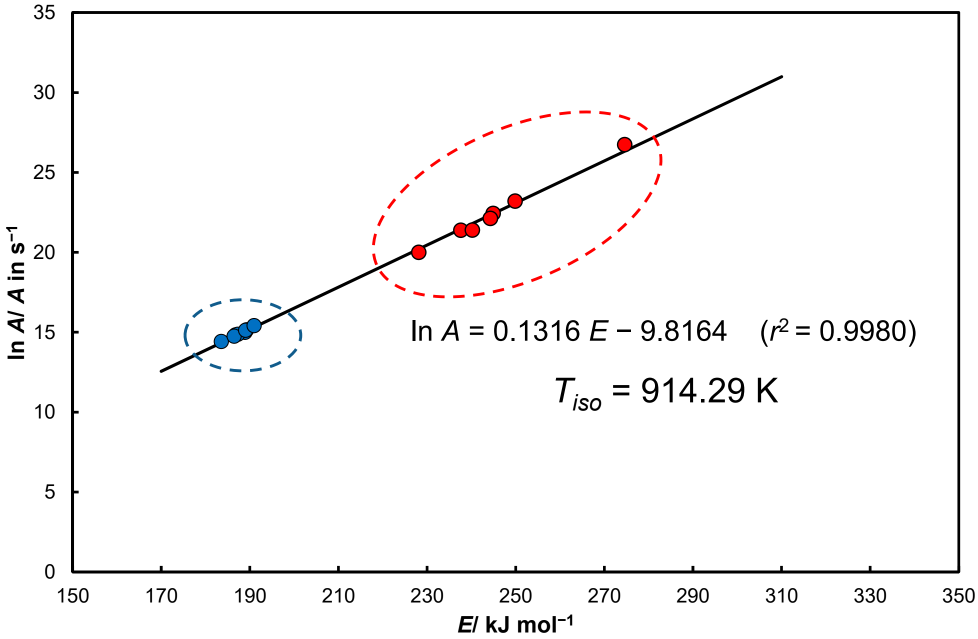

Figure 7. Typical KCE plot representing two groups of Arrhenius parameters pairs that form one IE.

The determined activation energies presented in Figure 7 form two resultant groups, in fact, they are combined in the form of one simple *KCE*. Results of the scoring method (much higher values–red) can be classified as quasi-isoconversional ($\alpha_0 \cong \text{const}$). On the other hand, values that are lower (blue) or close to the reference data (E = 191 kJ/mol, ln$A$ = 15.4/ A in s^{-1}) [35], e.g., Anderson) are determined for individual heating rate-dependent curves by the Coats−Redfern equation for a range of changes $\alpha \in [0.1 - 0.9]$.

For the data presented in Figure 7 for Equation (46) and $T_{iso} = 914.29$ K, $r^2 = 0.9980$ and temperatures: $T_{low} = 976$ K, $T_{high} = 1069.27$ K (for $\alpha \in [0.1 - 0.9]$, see [5]) and setting up $T^*, T_{high}, T_{hm} = 1020.51$ K for $N = 15$ and probability at least 99% (sl = 0.01) (Equation (48)):

$$CQF = 0.7017, \ \ CQF_{99} = 0.29 + \frac{1.41}{15^{0.57}}0.591$$

and from Equation (49):

$$K = 2.50$$

This result shows the reliability of the determined isokinetic temperature, which is ahead of the range of tested temperatures $(T_{iso} < T_{low})$. It therefore has the character of an extrapolated quantity.

4.5. Summary of Equations for Experimental Data

The resolution of the significance of the determined temperatures is described by three equations:

- typical *KCE* equation (Figure 7):

$$\ln A = \frac{E}{R \cdot 914.29} + \ln\left(5.455 \cdot 10^{-5}\right), \ r^2 = 0.9980 \tag{68}$$

- slope in Equation (57) provided in [43] concerning calcite dissociation from different references:

$$\Delta H^{+} = 1164.6 \cdot \Delta S^{+} + 342.22 \cdot 10^3 \tag{69}$$

- from the linear relationship between the parameters of the three-parameter equation, Table 5 (slope in Equation (70)):

$$A_1 = 896.29 \cdot A_2 + 31440 \;\; r^2 = 0.9977 \text{ for 7 heating rate} \tag{70}$$

However, according to Equation (45), for the constant temperature provided in Equation (68) $T_{iso} = 914.29$ K, a relatively large range is obtained: $\overline{k}_{iso} = 5.541 \cdot 10^{-5} \pm 9.899 \cdot 10^{-6}\, s^{-1}$.

In turn, we calculate only one compensation constant: $k_c = 0.0108\, s^{-1}$ from Equation (61) for the constants given in Equation (69). The value of this constant is much higher than the calculated average value of the isokinetic constant $\overline{k}_{iso}$. Thus, the intercept in *KCE* is literally a quantity that averages a wide range of variation in the kinetic constant at the isokinetic point.

Synoptic Figure 8 explains the discrepancy between T_0 and the experimentally obtained *KCE*. The analytical considerations take into account a very wide range of conversion degree variations up to the co-ordinate $[T_0;\ \alpha_0]$ while the research scope focuses on higher conversion degrees. By making selections in the base of single column matrix $\langle\alpha\rangle$ towards $\alpha \in [0.1 - 0.9]$, the slope, or activation energy, increases.

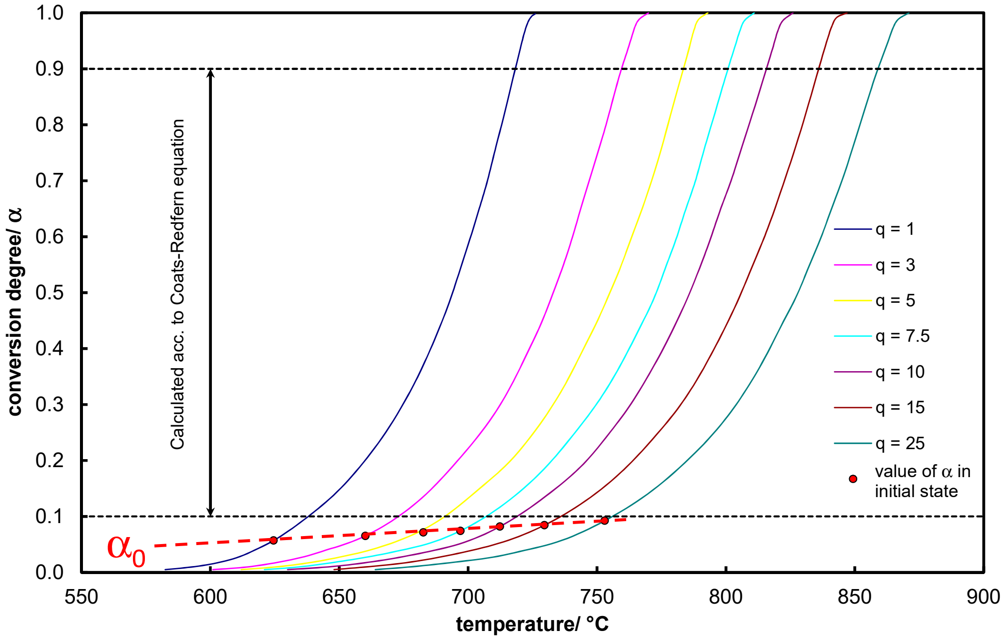

Figure 8. An illustrative comparison of using experimental data to determine the KCE equations.

According to Table 6, the relationships between the obtained temperature quantities are not very different from each other. The identity between T_{iso} and T_c is not confirmed (according to Equation (62)), and in turn $T_c = 1164.6$ K approaches $T_{eq} = 1172.4$ K [19]. The initial temperatures are consistent for the snapshots given in Tables 4 and 5 and, as it were, in their interval "absorb" the isokinetic temperature of Equation (68), which fulfills the indicator criterion of *CQF*, *K* [48,49].

The experimental data in terms of Equations (44) and (68) form a sequence of inequalities $T_c > T_{iso}$, while the exact isokinetic temperature is calculated from the formula: slope $= (RT_{iso})^{-1}$. In the correlation calculus using the ratio $1/T$ for the exact calculation of T was emphasized in the work [43], by which the accuracy of the numerical values between *KCE* and *EEC* (Equations (68) and (69)) should be distinguished, which was also pointed out in [55].

However, when too large a fluctuation of the assumed constancy of T_c is observed, it becomes necessary to carry out selection according to the proposal of Perez-Benito et al. [5,20]. The simplest approach is represented by inequality (71):

$$T_c > T \tag{71}$$

where T corresponds to temperature T_m in Equations (55) and (56) and is determined in [20] as a working temperature.

Table 6. Summary of temperatures determined for experimental data (T_{eq} = 1172.4 K [19]).

Equations/Table or Figures	T_0, K	T_{iso}, K	T_c, K	Remarks
(65)	-	914.29	-	-
(66)	-	-	1164.6	-
(67)	896.29	-	-	-
Table 4	876.3–990.6 (939.0)	-	-	-
Table 5	879.05–991.37 (939.88)	-	-	-
Figures A1–A4 for q = const	-	949.5–1060.6	-	T_{iso} is only of correlation−statistical meaning
Figures A1–A4 for α = const	-	1074.0–1298.4	-	T_{iso} is higher for isoconversional method (α = const.)

According to the findings of (71), the inequality is satisfied by Equations (68) and (69) in relation to the temperature of the maximum reaction rate, equal to $T = T_m = 1125.52$ K for a heating rate of 25 K/min (Table 5). In contrast, Equations (10) and (70) are closer to the definition of initial temperature. These findings remain consistent with the proposal of [43].

Following the concepts already used in Equations (46)−(49), the physicochemical sense of isokinetic and compensation temperature, which according to Equation (62) should be the same, it is most advantageous to verify in two steps based on the work [48,49] for statistically significant correlations.

It was proved experimentally that for chemical reactions of four chemically similar compounds (dissociation of hexacene dimers) the Eyring plot $(\ln(k/T)$ vs. $1/T)$ indicates the fact of occurrence of T_c several times in a narrow temperature range [56].

EEC expands our understanding of the little-studied quantitative aspects of organic reactions. Experimental evidence of its physical reality in a number of cross reaction series is considered through non-catalytic and pyridine-catalyzed reactions of aryloxiranes with organic acids of various classes. In the context of the compensation effect, there are transitions from one state of reaction systems in which the enthalpy term of the free activation energy acquires a zero value ($\Delta H^{+} = 0$, $\Delta G^{+} = -T\Delta S^{+}$), to another, in which the contribution to the free energy of activation of the entropy term disappears ($\Delta S^{+} = 0$, $\Delta G^{+} = \Delta H^{+}$) [57]. Mentioned in parentheses is that the thermodynamic states of the activation process are included in Equation (58).

On the other hand, from a physicochemical point of view, a very interesting example is presented in [46] concerning temperature programmed desorption (*TPD)*, when the surface coverage decreases with increasing temperature. Analyzing this phenomenon as a reversible process, while the isosteric heat of adsorption–once the entropy is determined–leads to *EEC* [6], the constant surface coverage condition is not respected–as is the case in isothermal sorption kinetic measurements–we observe a rather large scatter in terms of *KCE* [47].

4.6. Some Remarks to All the Elements

For dynamic conditions, the equation in differential form, Equation (8), is commonly recognized as the starting point for consideration. If the approximate form of the solution of Equation (8), referred to by the authors as the Coats−Redfern equation (Equation (9)), interacts with this equation, it leads to Equation (13). This equation has an identical mathematical structure, independent of the heating rate and pre-exponential factor. The consequences of analyzing the adoption of specific analytical forms of the integration constant open up new possibilities for comparison of the Arrhenius parameters obtained through different paths, including Vyazovkin's, discussed in detail in the book [31]. In contrast to isoconversion concepts, in this work one still stays with the classical variant ($q = \text{const}$) and for this possibility and for simulated "in silico" data the very important significance of the coordinate $[T_0, \alpha_0]$ is presented, thanks to which Equation (25) reproduces the activation energy E and also the constant $\ln A{\cdot}f(\alpha_0)$. For many models, $f(\alpha_0)$ can be calculated or simply ignored.

In relation to the proposal to determine the "elbow" point coordinate, based on the knowledge of higher order derivatives [38], the methodology has been simplified, which boils down to determining the isokinetic temperature from the constant in Equation (19) and calculating the initial transformation step from Equation (27) or (40).

On the other hand, consideration of simulated data does not provide a basis to demonstrate the existence of the *KCE*, which appears for experimental data. It is necessary not only to verify it statistically, but also using the *CQF* and K indicators via Equations (46)−(49) to give the isokinetic temperature a physicochemical sense.

In the association of works [5,20,21,43], the experimentally determined considered temperatures form a sequence, where T_{eq} denotes the thermodynamically determined equilibrium temperature of the reaction (Equation (6)), sometimes also called the inversion temperature:

$$T_0 \leftrightarrow T_{iso} \leftrightarrow T_c \leq T_{eq} \tag{72}$$

The current work proved that the temperatures T_{iso} and T_c are theoretically equal (compare Equations (44) and (62)), while the temperature sequence given in Equation (72) follows from many factors. These are: sample quality (mass, degree of purity, moisture content, crystalline/amorphous form, analysis conditions: isothermal/dynamic, heating rate, atmosphere, flow, reactor type) and workshop issues (variation of α, calculation techniques, distinguishing variants: $q = \text{const}$, $\alpha = \text{var}$ or $q = \text{var}$, $\alpha = \text{const}$). In light of these considerations, the isokinetic temperature T_{iso} is of lesser reliability than the initial temperature T_0 or even the compensation temperature T_c, which is implicit in the kinetic relationship.

As noted in [52], Equation (69) is derived from various sources, and Equation (68) is composed of correlation and point analysis–both equations involve the same reaction/process of thermal decomposition of calcite.

The omitted analysis of Equation (3) in conjunction with Equation (2) was hinted at in the paper [43].

5. What's Next?

From the point of view of the equations used, the starting point is the generally used Equation (8) for dynamic conditions and its most commonly used approximate Coats−Redfern solution (Equation (9)). The relation of Equations (8) with (9) leads to the differential Equation (11) with the analytical solution Equation (13). The condition of Equation (10) allows the determination of several equivalent forms of the integration constant in Equations (23) and (24). The final form of Equation (25) determines the activation energies using the heating rate (q) and initial temperature (T_0). In further steps, a new way of determining the coordinates $[T_0;\alpha_0]$ in Equations (40)−(43) is proposed. Further procedures use the relations of *KCE*, *EEC* and their constant characteristic temperatures against a narrowly variable initial temperature (T_0).

6. Conclusions

1. The relationship between *KCE* and *EEC* is mutually possible and it has been shown that the relationship $T_{iso} = T_c$ theoretically should occur. In light of these considerations, the isokinetic temperature T_{iso} is of less reliability than the initial temperature T_0 or even the compensation temperature T_c. The analysis for the same data of the thermal dissociation of calcite in nitrogen comes down to a sequence of temperatures $T_0 \leftrightarrow T_{iso} \leftrightarrow T_c \leq T_{eq}$.

2. The effect of the generally known Coats—Redfern solution influence on the differential kinetic equation for dynamic conditions (Equation (8)) and on the resulting isokinetic mathematical forms (Equation (13)) has been used. For in silico and experimental data in the case of thermal dissociation of simple solid chemical compounds, a relationship between the initial temperature T_0 and the heating rate has been demonstrated, which enables the determination of the Arrhenius equation parameters. An analytical way of determining the coordinate $[T_0,\ \alpha_0]$ based on the three-parameter equation considering the derivative at temperature T_0, $\mathrm{d}\alpha/\mathrm{d}\ln T \equiv 1$ has been proposed.

3. In solid-phase thermokinetic analysis, isokinetic relationships have been known for years. Equation (13) is independent of the heating rate and the activation energy is in turn invariant with the conversion degree. The integration constant in this equation can be expressed analytically in various ways. The possibility of its determination by quantities included in the coordinate $[T_0; \alpha_0]$, when $E = \mathrm{const}$, has been demonstrated. This type of viewpoint presents a different approach from the isoconversion methodology, for which $E = E(\alpha)$ is very often observed.

4. Using the parameters *CQF* and *K* as in [48,49], it has been shown that *KCE* in the physicochemical sense favors wide ranges of parameter variations of the Arrhenius law. The *CQF* index determines the reliability of even a very high probability of a linear relationship of the *KCE*. On the other hand, the position parameter *K*, assuming $r^2 = 1$, indicates that, for $-1 \leq K \leq 1$, the isokinetic temperature is within the range of tested temperatures and for the other values it has an extrapolative character.

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Nomenclature

$\boldsymbol{A_o}, \boldsymbol{A_1}, \boldsymbol{A_2}$	coefficients of the three-parametric Equation (40), A_1 in K,
A	pre-exponential factor, s^{-1},
B=2.08364·$10^{10}(\mathbf{K{\cdot}s})^{-1}$,	ratio of Boltzmann to Planck's constant,
C	integrals constant,
CQF	Compensation Quality Factor as in [48,49],
E	activation energy, J mol^{-1},
$\boldsymbol{f(\alpha)}, \boldsymbol{g(\alpha)}$	kinetics functions,
ΔG	free enthalpy, Jmol^{-1}
$H = 6.62607 \times 10^{-34}$ Js,	Planck constant
$\boldsymbol{H} = \Delta \boldsymbol{G}^{+}(\boldsymbol{T_c})$	free enthalpy of activation in T_c temperature, Equation (58), J mol^{-1},
ΔH	enthalpy, Jmol^{-1},
k,$\boldsymbol{k_{TST}}$	rate constant and dependent on T, s^{-1},
$\boldsymbol{k_B}$ = 1.38065·10^{-23} JK^{-1}	Boltzmann constant,
$\bar{\boldsymbol{k}}_{\boldsymbol{iso}}$	average value of the isokinetic constant, s^{-1},
K	position of coalescence as in [49], or position parameter,
m	coefficients,
n	exponent,
N	number of data,
p	pressure, Pa,
$\boldsymbol{r}^2, \boldsymbol{R}^2$	coefficients of linear or multiple determination,

R = 8.314 J (mol·K)$^{-1}$	universal gas constant,
q	heating rate, K s^{-1},
sl	significance level,
ΔS	entropy, J(mol*K)$^{-1}$,
T	absolute temperature, K,
T_0	initial temperature, K,
x	E/RT,
α	conversion degree, $0 < \alpha \le 1$,
$\langle\boldsymbol{\alpha}\rangle$	single column matrix,
β, γ	constants in Equations (1)–(3),
ν	stoichiometric coefficient.
Subscripts:	
c	compensation,
eq	equilibrium,
low, high, hm	relate to mean values of initial and final temperatures and their harmonic mean respectively,
i	ith value,
Iso	isokinetic values,
m	maximum of rate reaction/process,
Superscripts	
+	activation functions,
*	auxiliary quantity, Equations (A1), (A2),
g, s	gas, solid,
$\varnothing$	standard condition
Abbreviations	
EEC	Enthalpy−Entropy Compensation,
ICTAC	International Confederation for Thermal Analysis and Calorimetry,
KAS	Kissinger−Akahira−Sunose equation,
KCE	Kinetic Compensation Effect (also IKR, IE),
TPD	Temperature Programmed Desorption.

Appendix A

Table A1. List of kinetic functions as in [31] and approximation of the first term in Equation (14) $(0 < \alpha < 1)$.

Code	$f(\alpha)$	$g(\alpha)$	$f(\alpha)\cdot g(\alpha)$	$\ln g(\alpha)$ for α_0 *
P4	$4\alpha^{3/4}$	$\alpha^{1/4}$	4α	$\frac{1}{4}\ln\alpha_0$
P3	$3\alpha^{2/3}$	$\alpha^{1/3}$	3α	$\frac{1}{3}\ln\alpha_0$
P2	$2\alpha^{1/2}$	$\alpha^{1/2}$	2α	$\frac{1}{2}\ln\alpha_0$
P2/3	$\frac{2}{3}\alpha^{-1/2}$	$\alpha^{3/2}$	$\frac{2}{3}\alpha$	$\frac{3}{2}\ln\alpha_0$
D1	$\frac{1}{2}\alpha^{-1}$	α^2	$\frac{1}{2}\alpha$	$2\ln\alpha_0$
F1	$1-\alpha$	$-\ln(1-\alpha)$	$-(1-\alpha)\ln(1-\alpha)$	$\ln\alpha_0$
A4	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$	$4(1-\alpha)[-\ln(1-\alpha)]$	$\frac{1}{4}\ln\alpha_0$
A3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$	$3(1-\alpha)[-\ln(1-\alpha)]$	$\frac{1}{3}\ln\alpha_0$
A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$	$2(1-\alpha)[-\ln(1-\alpha)]$	$\frac{1}{2}\ln\alpha_0$
D3	$\frac{3}{2}(1-\alpha)^{2/3}\left[1-(1-\alpha)^{1/3}\right]^{-1}$	$\left[1-(1-\alpha)^{1/3}\right]^2$	$\frac{3}{2}(1-\alpha)^{2/3}\left[1-(1-\alpha)^{1/3}\right]$	$2\ln(\alpha_0/3)$
R3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}\left[1-(1-\alpha)^{1/3}\right]$	$\ln(\alpha_0/3)$
R2	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}\left[1-(1-\alpha)^{1/2}\right]$	$\ln(\alpha_0/2)$
D2	$[-\ln(1-\alpha)]^{-1}$	$\alpha+(1-\alpha)\ln(1-\alpha)$	$\frac{\alpha+(1-\alpha)\ln(1-\alpha)}{[-\ln(1-\alpha)]}$	$2\ln\left(\frac{\alpha_0}{\sqrt{2}}\right)$

* Maclaurin expansion was used, for model D3–after squaring. Stopped at the first term of the equation.

Analysis of *KCE* for Experimental Data

The *KCE* resulting from the analysis of the experimental data on the thermal dissociation of calcite in nitrogen is presented in Figure A1. While Figure A1a presents the

KCE resulting from the analysis of data according to Equation (35) for seven different heating rates. Figure A1b presents the KCE for six different heating rates, omitting data for q = 1/60 K·s^{-1}.

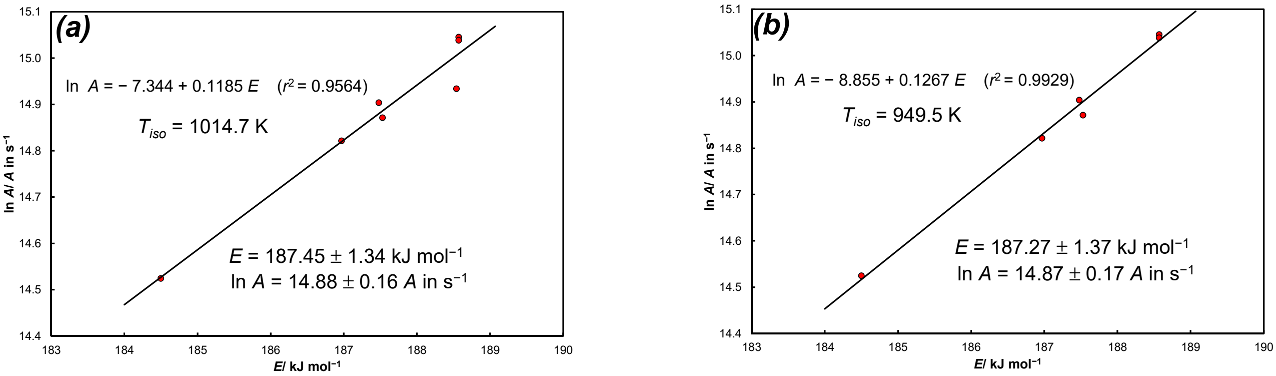

Figure A1. *KCE* for experimental data of thermal dissociation of calcite in nitrogen: (**a**) source: Equation (35), N = 7 heating rates, T_{iso} = 1014.7 K, E = 187.45 ± 1.34 kJ·mol^{-1}, ln$A$ = 14.88 ± 0.16 (A in s^{-1}), *sl* = 0.0(3)14; (**b**) source: Equation (35), N = 6 heating rates (data for q = 1/60 K·s^{-1} is omitted), T_{iso} = 949.5 K, E = 187.27 ± 1.37 kJ·mol^{-1}, ln$A$ = 14.87 ± 0.17, (A in s^{-1}). *sl* = 0.0(4)19.

Despite the small variability of the parameters of the Arrhenius law, they meet the *KCE* at a sufficient level of significance. The average results provided in the description of Figure A1 are consistent with the data presented by Anderson [21] for the 0th order kinetics (E = 191 kJ·mol^{-1}, ln$A$ = 15.4/A in s^{-1}).

The average values obtained with the use of the kinetic function (37) are slightly different, as presented in Figure A2.

In relation to the analysis presented in Figure A2. the isoconversional approach of Equation (37) for the average values of E and ln A is not too much of an outlier and falls within the ranges presented in [21] but with an unsatisfactory coefficient of determination. However, it should be noted that the calculated isokinetic temperatures differ significantly depending on the data selection method. In the case of experimental research, when we analyze only the available range of increase in the conversion rate from temperature (here $\alpha \in [0.1 - 0.9]$) a different type of *KCE* is observed for the constant heating rate analyses and a different type for the isoconversional method. The position presented in [5] is thus confirmed.

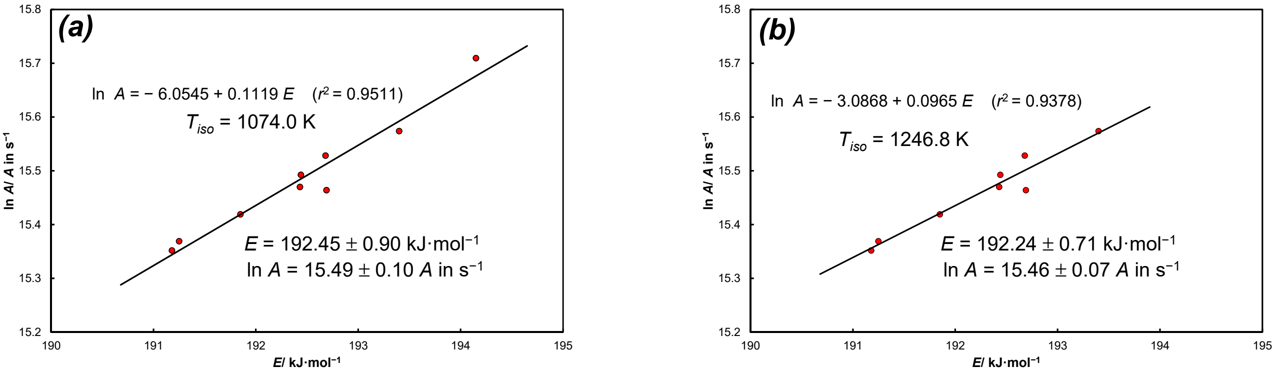

Figure A2. *KCE* for experimental data of thermal dissociation of calcite in nitrogen: (**a**) source: Equation (37), N = 9 positions α = const., T_{iso} = 1074.0 K, E = 192.45 ± 0.90 kJ·mol^{-1}, ln$A$ = 15.49 ± 0.10 (A in s^{-1}), *sl* = 0.0(5)8; (**b**) source: Equation (37), N = 8 positions α = const. (data for α = 0.1 is omitted), T_{iso} = 1246.8 K, E = 192.24 ± 0.71 kJ·mol^{-1}, ln$A$ = 15.46 ± 0.07 (A in s^{-1}), *sl* = 0.0(4)8.

Figures A3 and A4 show the *KCE* resulting from the analysis of experimental data of thermal dissociation of calcite in nitrogen from Equations (36) and (38).

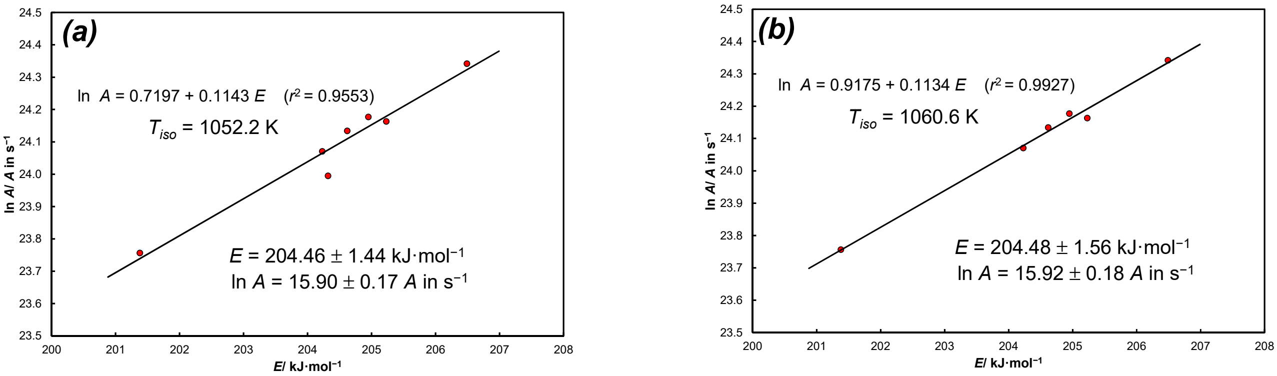

Figure A3. *KCE* for experimental data of thermal dissociation of calcite in nitrogen: (**a**) source: Equation (36), 9 positions for α = const and N = 7 heating rates, T_{iso} = 1052.2 K, E = 204.46 ± 1.44 kJ·mol^{-1}, ln$A$ = 15.90 ± 0.17 (A in s^{-1}), *sl* = 0.0(3)15; (**b**) source: Equation (36), 9 positions for α = const and N = 6 heating rates (data for q = 1/60 K·s^{-1} is omitted) T_{iso} = 1060.6 K, E = 204.48 ± 1.56 kJ·mol^{-1}, ln$A$ = 15.92 ± 0.18 (A in s^{-1}), *sl* = 0.0(4)2.

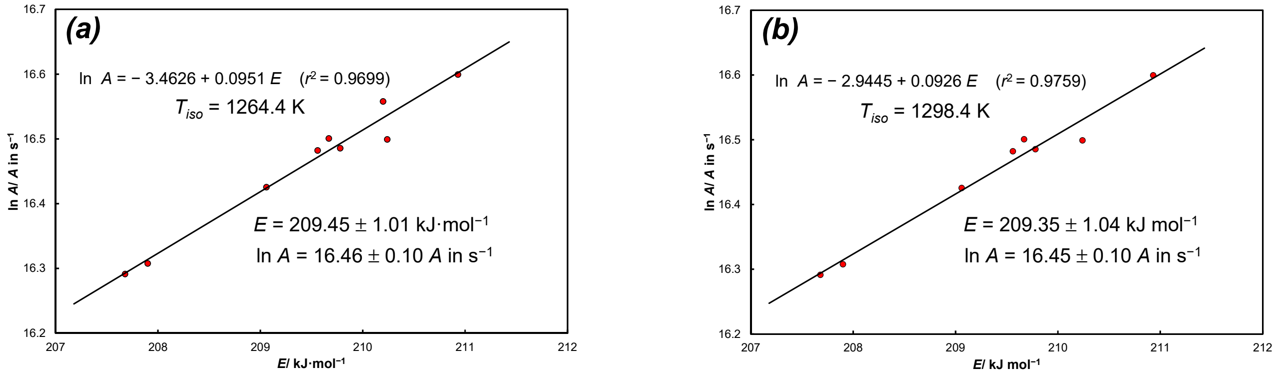

Figure A4. *KCE* for experimental data of thermal dissociation of calcite in nitrogen: (**a**) source: Equation (38), 7 heating rates and N = 9 positions for α = const, T_{iso} = 1264.4 K, E = 209.45 ± 1.01 kJ·mol^{-1}, ln$A$ = 16.46 ± 0.10 (A in s^{-1}), *sl* = 0.0(5)1; (**b**) source: Equation (38), 7 heating rates and N = 8 positions for α = const (α = 0.1 is rejected, T_{iso} = 1298.4 K, E = 209.35 ± 1.04 kJ·mol^{-1}, ln$A$ = 16.45 ± 0.10 (A in s^{-1}), *sl* = 0.0(5)4.

Physicochemical sense of isokinetic temperature

Temperature T^* in Equation (46) follows from implication, when:

$$\left|\frac{1}{T_{min}} - \frac{1}{T_{high}}\right| < \left|\frac{1}{T_{min}} - \frac{1}{T_{low}}\right|.\text{then } T^* = T_{low} \tag{A1}$$

$$\left|\frac{1}{T_{min}} - \frac{1}{T_{high}}\right| > \left|\frac{1}{T_{min}} - \frac{1}{T_{low}}\right|.\text{ then } T^* = T_{high} \tag{A2}$$

In Equation (48), the quantity $0.29 \approx 1 - \sqrt{\frac{1}{2}}$ is the *CQF* threshold for an infinite number of N measurements.

The individual temperatures denote the test temperature interval: T_{low} is the arithmetic mean of the initial temperatures, T_{high} is the mean temperature of the end of the interval and T_{hm} is the harmonic mean of the temperatures T_{low}. T_{high}.

For Equation (46) limit values are observed:

- in the simplest variant: $r^2 \equiv 1\ CQF = 1$.

$$\text{when } T^* = T_{iso}.CQF = 1 - \sqrt{r^2} = 1 - r \tag{A3}$$

which means that the isokinetic temperature is the beginning/end of the temperature interval.

$$\text{when } \lim_{T^* \to \infty} .CQF = 1 - \sqrt{1 - r^2} \tag{A4}$$

$$\text{when } \lim_{T^* \to 0} .CQF = 1 \tag{A5}$$

it represents the very favorable case where the test range of the temperature interval tends towards very low temperatures in relation to T_{iso}.

In turn, the position parameter K indicates the location of T_{iso} relative to the range of temperatures used–Figure A5.

Always $T_{hm} < \frac{T_{low} + T_{high}}{2}$ thus in Equation (49) K = 0 is parallel when $T_{hm} = \frac{T_{iso}}{r^2} = T_{min}$ (Equation (47)).

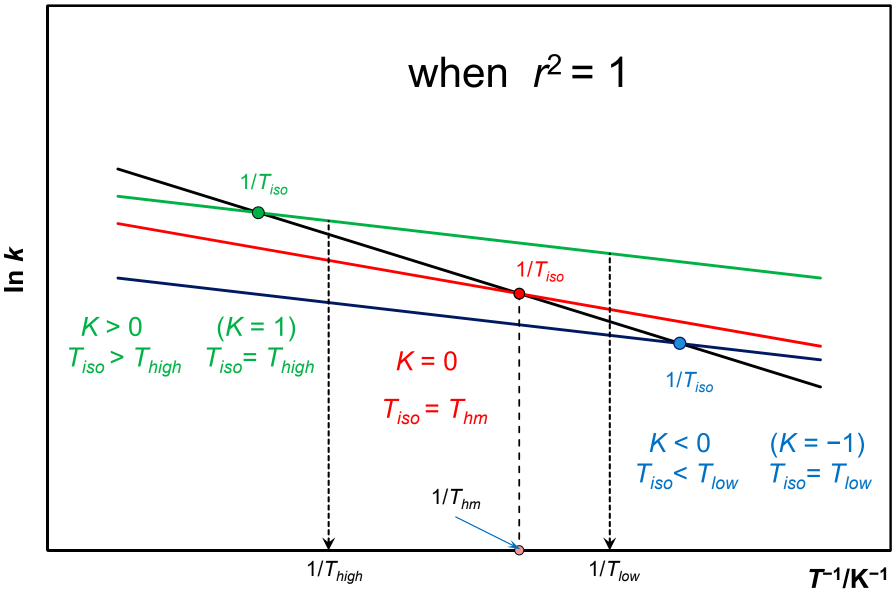

Figure A5. Arrhenius plot with indication of location of T_{iso} in relation to the temperatures analyzed, taking into account data from [48,49] only for the case where r^2 = 1.

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