

## Article

# Practical Aspects of the Analysis of Thermal Dissociation and Pyrolysis Processes in Terms of Transition State Theory

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**Abstract:** The practical implementation of transition state theory (TST) commonly assumes equivalence between theoretical and experimentally determined rate constants, represented by Arrhenius parameters—the activation energy and pre-exponential factor. Here, we employed the General Rate Equation (GRE) to analyse solid–gas-phase thermolysis in two paradigms: mass loss (e.g., calcite decomposition) and mass gain (e.g., methane pyrolysis leading to solid carbon formation). By partitioning the Gibbs free energy of activation into forwards and reverse contributions, plus an additional term accounting for concurrent physical phenomena (notably nucleation and diffusion-viscosity effects), we derived an empirical universal expression relating both Arrhenius parameters and  $\Delta G^+$  across 500–1500 K. We further demonstrate the utility of the isokinetic temperature for interpreting cases where only Kinetic Compensation or Enthalpy–Entropy Compensation effects are observed. This framework unifies kinetic and thermodynamic descriptions of complex thermolysis processes.

**Keywords:** general rate equation (GRE); transition state theory (TST); thermolysis; activation; nucleation; equilibrium temperature; isokinetic temperature



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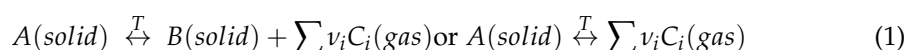
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## 1. Introduction

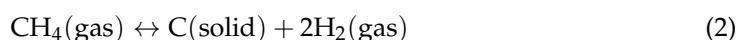
Thermal dissociation is the reversible decomposition of molecules into smaller molecules or atoms under the influence of elevated temperature, resulting in the breaking of the weakest bonds. Pyrolysis is a degradation process and can be defined as the splitting of large molecules of a chemical compound into smaller, or at least simpler, molecules under the influence of temperature in the absence of oxygen or other oxidizing agents. Thermal dissociation applies to inorganic compounds as well as to salts of organic acids and bases, while pyrolysis is a general term and includes mixtures of both organic and inorganic substances. The sharp boundary between these terms necessitates a number of additional terms, the most useful of which is probably the diagram illustrating thermal chemical transformation, hereafter referred to as thermolysis [1]:



where the directions of the transformation are unified in a forwards–backwards sense, and  $v_i$  is the stoichiometric coefficient.

In any thermal process undergone by a solid substrate A, the products may be in the solid, liquid, or gaseous phase—a characteristic feature of pyrolysis.

A special case of reaction scheme (1) may be the process of thermal degradation of gases, the most interesting in recent years being the thermolysis of methane:



Notation (2) is the simplest and most encountered on an industrial scale. The network of possible reaction pathways in which methane is converted into various gaseous components and solid carbon—terminating at  $\text{C}_{5-6}$  hydrocarbons—is described in [2]. As a subsequent type of this process, pyrolysis of olefins should be regarded. Here, hydrocarbons, mainly saturated hydrocarbons, are passed through a tubular reactor at a high temperature (700–950 °C). In addition to olefins, the main product of olefin pyrolysis is hydrogen ( $\text{H}_2$ ) and the aromatic fraction (mainly benzene).

Between 2023 and 2025, four ITPE papers addressed thermal dissociation and pyrolysis from a practical standpoint, employing fundamental kinetic and thermodynamic Equations, including those related to activation thermodynamics [3–6]. In [3], particular emphasis was placed on a set of temperature functions that delineated a series of relationships between isokinetic and equilibrium temperatures, while [4] presented elements of transition state theory in the form of balances of the free energy for the process of thermal dissociation of selected solid-state compounds. Consequently, [5] undertook a literature review on the thermal decomposition of methane from the perspective of kinetic analysis, taking into account the Kinetic Compensation Effect (KCE) and Enthalpy–Entropy Compensation (EEC) for thermodynamic activation functions. Finally, a free energy balance (for calcite) with kinetic activation analysis of the nucleation of the resulting solid phase ( $\text{CaO}$ ) was described in [6].

Given the multidisciplinary nature of the topic discussed herein, the authors provide here only a brief literature review, which is expanded as theoretical and practical concepts are developed in subsequent sections.

## 2. Purpose of the Work

Drawing on [3–6], we propose a practical approach to the thermal decomposition of complex solid-phase substances—including methane dissociation—via the General Rate Equation. The starting point is the General Rate Equation (GRE), characteristic of the solid-phase conversion degree, defined in chemical terms and then with an imposed thermodynamic constraint. The kinetic model determines the rate constant and its properties. Going further, this paper discusses applicability of equilibrium ( $T_{eq}$ ) and isokinetic temperature ( $T_{iso}$ ). The latter ( $T_{iso}$ ) is most commonly associated with KCE and EEC. Relevant relationships between isokinetic and equilibrium temperatures are presented in [3]. An analysis of the literature, as well as the authors' own work [3–6], has shown that the central point of idealised elementary reactions is the isokinetic temperature instead of the commonly used temperature of the maximum conversion rate.

The pyrolysis process in this paper is considered on the basis of the methane molecule, while for the thermolysis, the considerations are supported by data and experiments known for calcite.

## 3. Theory

Examples of thermal dissociation, pyrolysis, or direct thermolysis are closely related to the possibility of searching for kinetic models in the category of the degree of conversion ( $\alpha$ ) of the substance A (solid) as the dependent variable with respect to time or under dynamic

temperature conditions. For the reactions/processes covered by the notations (1,2), the General Rate Equation (GRE) can be used in the form of  $\alpha$  as is written in [7,8]:

$$r = \frac{d\alpha}{dt} = k(T)f(\alpha), \quad T = \text{constant} \quad (3)$$

where  $r$  stands for reaction rate. Under isothermal conditions, the term is associated with the kinetic function  $f(\alpha)$  multiplied by a proportionality factor, called the rate constant.

The GRE, when fitted with an additional term expressing a thermodynamic constraint, has the form [9–12]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \cdot [1 - \exp\left(\frac{\Delta G}{RT}\right)] \quad (4)$$

Given that  $\Delta G$  is Gibbs free energy, we can also write the following:

$$\Delta G = RT \ln \frac{K_\alpha}{K} \quad (5)$$

When  $K_\alpha \leq K$ , then  $\Delta G \leq 0$ ,  $\text{J} \cdot \text{mol}^{-1}$ , and the substitution of Equation (5) to Equation (4) leads to the following form:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \left[1 - \frac{K_\alpha}{K}\right] \quad (6)$$

In Equations (4) and (5),  $K$  is the thermodynamic equilibrium constant, while  $K_\alpha$  has the same mathematical structure as the constant in the denominator. Note that here it refers to the instantaneous conversion degree. The expression  $[1 - \frac{K_\alpha}{K}] = DFE$  (Distance from Equilibrium) represents distance from equilibrium or far from equilibrium. When  $\frac{K_\alpha}{K} \rightarrow 1$ , the reaction rate  $\frac{d\alpha}{dt} \rightarrow 0$  and, consequently, according to Equation (5),  $\Delta G = 0$ . The above implies the classical expression for an equilibrium of a reaction:

$$\Delta_r G^\circ = -RT \ln K \quad (7)$$

which, followingly, is equivalent to van't Hoff's equilibrium equation for isobaric conditions:

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta_r H^\circ}{RT^2} \quad (8)$$

For the simplest case of reaction (1), i.e., for a single gas product, its thermodynamic equilibrium constant can be expressed as [6]:

$$K = \left(\frac{P_{eq}}{P^\circ}\right)^{\nu_i} \quad (9)$$

Thus, the instantaneous rate constant is given as:

$$K_\alpha = \left(\frac{P_i}{P^\circ}\right)^{\nu_i} \quad (10)$$

and to simplify the notation,  $k(T)$  can be expressed as  $k$ , and thus, Equation (6) can take the following form:

$$\frac{d\alpha}{dt} = kf(\alpha) \left[1 - \left(\frac{P_i}{P_{eq}}\right)^{\nu_i}\right] \quad (11)$$

where  $P_i$  is the partial pressure of the gaseous product formed in the reaction/process. Most research in this area has been devoted to the contributions of  $\text{CO}_2$  and steam in the field of thermolysis of hydrates. The series of publications by Prof. Koga et al. [13–26] is based not only on Equation (11) but also on other algebraic relations of pressure ( $P_i$ ) and

equilibrium pressure ( $P_{eq}$ ) [26]. The Controlled Transformation Rate Thermal Analysis (CRTA) emphasises the reversibility of the reaction/process, creating new possibilities for interpreting the Kinetic Compensation Effect (KCE) in terms of phenomenological thermodynamics what we symbolically indicate as  $T_{iso} \rightarrow T_{eq}$  (e.g., intercept: Equation (22) in [26]).

The concept of  $T_{iso} \rightarrow T_{eq}$  has been echoed in earlier work [3,26–28]. Experimental demonstration of how CRTA combines elements of kinetics captured by KCE variation, with standard thermodynamic functions can be found in [26].

On the other hand, when analysing the kinetics of reaction (2) as a reversible catalytic-free elementary reaction leading to only one gaseous product, hydrogen, the equation in the category of molar fraction of pure methane ( $x$ ) can be written as [5]:

$$-\frac{dx}{dt} = k_1x - k_{-1}(1-x)^2, T = \text{constant} \quad (12)$$

For the conversion degree of methane and given the following assumptions ( $k_1$  for forwards reaction and  $k_{-1}$  for backwards reaction), we can see that:

$$K = \frac{k_1}{k_{-1}} \quad (13)$$

$$x = \frac{1-\alpha}{1+\alpha}, 1-x = \frac{2\alpha}{1+\alpha} \quad (14)$$

Followingly, for pure methane as a substrate, the following can be expressed:

$$\frac{d\alpha}{dt} = \frac{k_1}{2} \left[ 1 - \left( \frac{\alpha}{\alpha_{eq}} \right)^2 \right] \quad (15)$$

In the same paper, the authors have also expressed Equation (15) in the following form:

$$\frac{d\alpha}{dt} = k_1 \frac{1-\alpha^2}{2} \left[ 1 - \frac{K_\alpha}{K} \right] \quad (16)$$

where

$$K_\alpha = 4 \frac{\alpha^2}{1-\alpha^2}, K = 4 \frac{\alpha_{eq}^2}{1-\alpha_{eq}^2} \quad (17)$$

To keep the discussion concise, the transition from Equation (12) to Equation (16) is presented in Appendix A of this paper.

With respect to the GRE, Equation (16) hypothetically indicates the existence of a kinetic function  $f(\alpha) = \frac{1-\alpha^2}{2}$ , which, in this form, is not found in solid-phase thermolysis processes. This fact can be verified, since different notations of the function  $f(\alpha)$  (from the group denoted by R, D, A with the corresponding numbers) and detailed recommendations for solid-phase thermolysis are presented in [29] (292 entries cited). The authors also presented the thermodynamic constraints of the GRE in several forms, including the factor  $\frac{P_i}{P_{eq}}$ .

The interpretation of Equations (11) and (16) differs in the nature of the phenomenon. In the former, DFE/CRTA is an additional cognitive factor, which complements the state of knowledge, while in the latter, it is a sine qua non condition. As the substrate (methane) is diluted and the temperature increases, the equilibrium conversion degree can be neglected in the equations [5]. Moreover, the initial case (1) demonstrates an occurrence of mass loss, while the subsequent case (2) exhibits a phenomenon of mass gain. For complex processes, e.g., the pyrolysis of biomass, plastics or coals, or chars, a resultant picture is observed where the remaining solid is slightly enriched in carbon or minerals. Therefore, in the instance of complex substrates where the resulting gases may undergo further

decomposition processes, the determination of a reliable isokinetic temperature ( $T_{iso}$ ) offers the possibility to replace the thermodynamically defined equilibrium temperature ( $T_{eq}$ ). According to Krug's [30] theorem on the equality of rate constant with thermodynamic equilibrium constant for isokinetic temperature, an approximation  $T_{iso} = T_{hm}$ , where  $T_{hm}$  is the harmonic mean of the measurements, is proposed in the interpretation of the linear relationship of Enthalpy–Entropy Compensation (EEC).

More recent work has addressed the issue of the reliability of isokinetic temperature verification by Griessen et al. [31,32], including the use of an easily determined harmonic temperature.

According to Equation (17), a conversion degree appears both in the kinetic function and in the thermodynamic constants contained in Equation (6); the combination of the product  $f(\alpha) \cdot [1 - \frac{K_p}{K}]$  opens new possibilities in the field of GRE considerations, as this product indicates the connections between kinetics and phenomenological thermodynamics.

According to [6], in simple cases, e.g., when a single gas product is formed, Equation (11) can be represented as [10], where  $v_i$  is the stoichiometric ratio of gaseous products:

$$\frac{d\alpha}{dt} = kf(\alpha)[1 - (\frac{\alpha}{\alpha_{eq}})^{v_i}] \quad (18)$$

In everyday research practice, DFE is usually neglected, especially when the GRE is converted to dynamic conditions and heating rate  $q = \frac{dT}{dt}$ , the equation for variable temperature is as follows:

$$\frac{d\alpha}{dT} = \frac{k}{q}f(\alpha)[1 - (\frac{\alpha}{\alpha_{eq}})^{v_i}] \quad (19)$$

As temperature increases, both conversion degree and equilibrium conversion degree increase, but formally  $\alpha \leq \alpha_{eq}$ .

#### 4. Rate Constant by Arrhenius

The structures of the GRE Equation link the reaction rate to the kinetic function and to a possible DFE constraint. According to this idea, the rate constant depends on the relationship  $T - P$ ; however, it also remains dependent on the variables used in the kinetic forms of  $f(\alpha)$ , as well as on other influencing factors such as those resulting from the way the reaction/process is carried out. Assuming standard conditions for pressure ( $P^\circ = \text{constant}$ ), the temperature dependence of the rate constant is expressed by the classical Arrhenius Equation of 1889 [33]:

$$k = A \cdot \exp(-\frac{E}{RT}) \quad (20)$$

where  $A$  in the simplest way is described by the relation  $A = \text{Const} \cdot T^b$  with the exponent  $b$ , taking values in the range from  $-1.5$  to  $-2.5$  [10–12,34–37]. Other concepts, referred to as non-Arrhenian [7], including those involving more complicated algebraic expressions, are also possible [34,35,38,39].

Given the close links with other theories in this area, the following modified or explicitly non-Arrhenius form of the Equation for  $k$  [39–43] is worth quoting here:

$$k = A \cdot (1 - d \frac{\varepsilon}{RT})^{\frac{1}{d}} \quad (21)$$

In this view, it can be seen that as  $d \rightarrow 0$  then  $\varepsilon \rightarrow E$ , and from the literature [39], it follows that  $\varepsilon \gg E$ . According to [42], for the parameter  $d < 0$ , there is a possibility to transform Equation (21) to deformed transition state theory (TST) or other forms related to the tunnelling effect proposed in [41].

## 5. Rate Constant by Eyring

Derived from quantum mechanics and statistical thermodynamics, in 1935, Eyring proposed the absolute rate constant [44], and to this day, this remains the most frequently cited position in the literature defining transition state theory (TST), even though his formulations are complex from an energy point of view. Nevertheless, the following practical forms of the theory's greatest achievements (for  $P^\circ = \text{constant}$ ) can be extracted from the very advanced layers of the text [44,45]. In the following parts of the paper the thermodynamic activation functions given as phenomenological functions are distinguished using the symbol  $+$ :

$$k_{TST} = \chi \frac{k_B T}{h} K^+ \quad (22)$$

$$\Delta G^+ = -RT \ln K^+ \quad (23)$$

$$\Delta H^+ = RT^2 \frac{\partial \ln K^+}{\partial T} \quad (24)$$

$$\Delta S^+ = \frac{\Delta H^+ - \Delta G^+}{T} \quad (25)$$

Using Equation (23), Equation (22) is presented in its most common form:

$$k_{TST} = \chi \frac{k_B T}{h} \exp\left(-\frac{\Delta G^+}{RT}\right) \quad (26)$$

whereby the classic Gibbs free energy of activation relationship applies:

$$\Delta G^+ = \Delta H^+ - T\Delta S^+ \quad (27)$$

In general, Equation (22) assumes the transition function  $\chi = 1$ , but in its simplest form it can also be expressed in the following way, as accepted by Eyring [45]:

$$\chi = 1 + \frac{1}{24} \left( \frac{h\nu}{k_B T} \right)^2 \quad (28)$$

For contrast, Wigner noted that [46]

$$\nu = \frac{k_B T}{h} = B \cdot T \quad (29)$$

where  $\nu$  stands for vibrational/oscillation frequency, and the condition  $\nu \ll B \cdot T$  must be satisfied. Much later, Henderson [47] confirmed that the frequency of crossing the barrier is a universal constant  $\frac{k_B T}{h}$  ( $T = \text{constant}$ ) independent of the nature of the reactants and type of reaction. Surprisingly, over the years, it has been found out that many time-dependent processes, such as viscosity, diffusion, plasticity, or electrical conduction can be related to  $B \cdot T$  [47], where  $B = \frac{k_B}{h} = 2.08364 \cdot 10^{10} \text{ (K} \cdot \text{s)}^{-1}$ .

To simplify when  $\chi = 1$ , Equations (26), (27), and (29) take a practical form for calculations of:

$$k_{TST} = BT \cdot \exp\left(-\frac{\Delta H^+}{RT} + \frac{\Delta S^+}{R}\right) \quad (30)$$

The interpretation of the TST according to [44] and, more recently, as given in [48] assumes a course of reactions:



in which the transition state is a surprising and new take on the classical approach that considers the existence of an activated complex. For an elementary reaction, according to

Equations (22)–(24), the characteristic feature is the quasi-equilibrium activation constant  $K^+$ , and according to [4], the initiation of the reaction is assumed according to first-order kinetics. From the work of [49], from 1937 onwards, the consideration of the solid phase is proposed when analysing this topic, and it should be noted that in later years, the general TST equation is also known as Eyring–Evans–Polanyi.

For the course of reaction/process (1), the scheme Equation (31) is reduced to the form:



The state characterised as  $K^+$  is difficult to imagine, although, as more recent work indicates, its description/representation is possible for calcite [6,50], as well as for some other inorganic salts [4].

A number of papers dealing with TST [3–6,41–63], at varying levels of sophistication, consider energy relations, including those linking to activation energy. The most important finding is the assumption of the following equality [4,48,61]:

$$k = k_{TST} \quad (33)$$

It should be noted that Equation (33) is not universal, and that the occurrence of such equivalence is determined both by the identifiability of the elementary reaction, the constant conditions  $T - P$ , the range of temperatures tested, as well as the kinetic models adopted on the GRE and TST sides. Figure 1, reproduced below, shows an example for a reaction of the type  $F + H_2 = FH + H$  [60], illustrated using Equation (33).

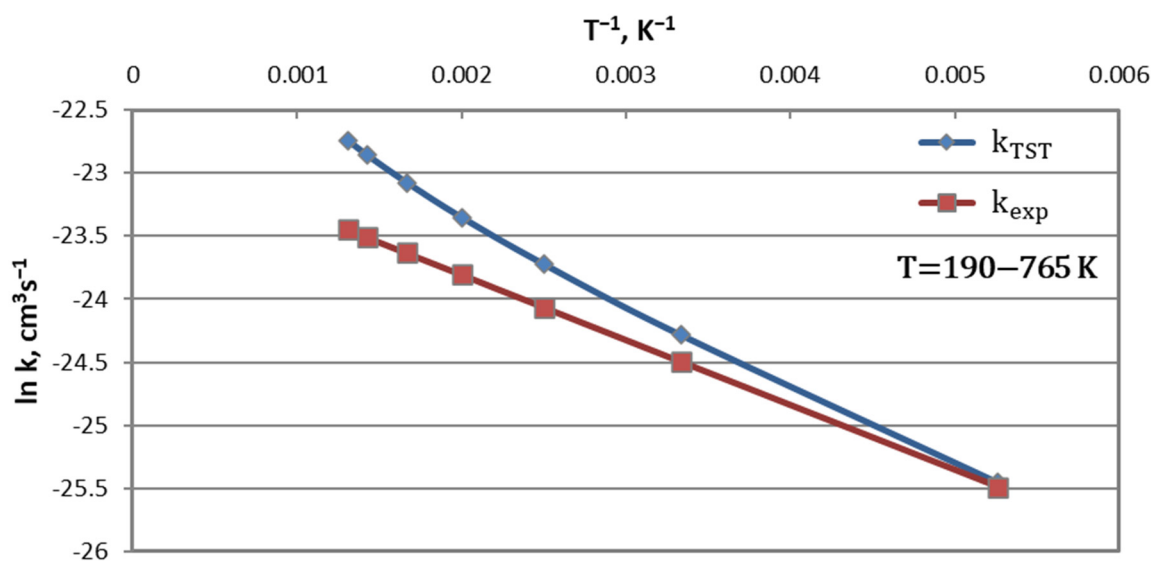


**Figure 1.** Comparison of rate constant according to the TST model (blue) with experimental results (red)  $k = 1.29 \cdot 10^{-10} \exp\left(-\frac{517.17}{T}\right)$ ,  $cm^3 s^{-1}$  for the reaction  $F + H_2 = FH + H$  (data source: [60]).

From Figure 1, it can be seen that according to Equation (33), the equality of the reaction rate constants occurs at low temperatures. Agreement with experimental results is obtained by modifying the TST model using Equation (21) for the expression in parentheses and by describing the exponent  $d$  as a temperature-dependent variable. However, one must consider that the activation energy presented here is very small  $E = 4.30 \text{ kJ} \cdot \text{mol}^{-1}$ .

Leaving aside the details of dissecting the relation Equation (33) analogous to the system of Equations (23)–(25) with Equation (26), we obtain [4,48]:

$$\Delta G^+ = RT \ln \frac{BT}{k} \quad (34)$$

or, after taking Equation (20), into account:

$$\Delta G^+ = E + RT \ln \frac{BT}{A} \quad (35)$$

After differentiating Equation (33), we know that

$$\Delta H^+ = E - RT \quad (36)$$

and the combination of Equations (20), (25) and (34) results in:

$$\Delta S^+ = R \left[ \ln \left( \frac{A}{BT} \right) - 1 \right] \quad (37)$$

In relation to Equations (34)–(36), one encounters a number of different modified forms, e.g., where Equation (36) is presented as:

$$\Delta H^+ = E - nRT \quad (38)$$

Here,  $n = 1$  (single-molecule reactions),  $n = 2$  (two-molecule reactions), and  $n = 0$  refer to phenomena with a high proportion of physical processes, e.g., polymerisation [64], decompositions occurring at low temperatures (energetic materials) [65], or in general processes where the product  $RT$  can be ignored [48].

Therefore, for  $n = 0$  and equality  $\Delta H^+ = E$ , Equations (27) and (37) take the following form:

$$\Delta G^+ = E - T\Delta S^+ \quad (39)$$

$$\Delta S^+ = R \ln \left( \frac{A}{BT} \right) \quad (40)$$

After substituting Equation (40) to Equation (39), Equation (35).

The fundamental significance is represented by Equation (33), which holds for  $\chi = 1$  and equates Equations (20) and (22). This leads to:

$$K^+ = \frac{k}{BT} \quad (41)$$

where rate constant  $k$  is the classical Arrhenius approach used in Equation (20).

After logarithmisation and then differentiation with respect to temperature, we obtain (for  $P^\circ = \text{constant}$ ):

$$\frac{d \ln K^+}{dT} = \frac{E}{RT^2} - \frac{1}{T} \quad (42)$$

After insertion into Equation (24) and rearrangement, one obtains Equation (36) (or when  $n = 1$ , Equation (38)).

For the purposes of this analysis, Equation (41) allows the applicability of the TST to be extended. For this notion to be true, it is sufficient that  $K^+ > 0$ , but on a numerical scale, the limit of sensibility of such an approach is unknown. According to Equation (41), the order of magnitude of  $K^+$  is on the scale of  $10^{-13}$  to  $10^{-17}$ , and the decomposition of solid energetic materials is of the order from  $10^{-13}$  to  $10^{-14}$  [4,5].

Further analysing the denominator of Equation (41), it is worth noting that for the special case of  $\nu = BT_{iso}$  [66,67], this inverse of  $1/\nu$  is the mean lifetime of the transition-state (TS) [60]. For example, for calcite  $\nu = 10^{13} \text{ s}^{-1}$  [4], so the mean lifetime of the TS in

this case is  $10^{-13}$  s; thus, we are wondering in the realm of infinitesimally small quantities. This kind of reasoning leads also to the following illustrative relationship [60]:

$$K^+ = k \cdot t_v \quad (43)$$

## 6. Relation Between TST and Free Energy

### 6.1. Approach to $\Delta_r G^\ominus$ No. 1

A detailed proposal for the determination of free energy as a relation between phenomenological thermodynamics and activation is presented in [4–6]. However, for the purposes of the present analysis, the relationship between equilibrium constant and rate constant forwards–backwards can be used as a basis, and thus in logarithmic form Equation (13), can be written as:

$$\ln K = \ln k_1 - \ln k_{-1} \quad (44)$$

and this leads to a relationship [4]:

$$\Delta_r G^\ominus = \Delta G^+ - \Delta_{-1} G^+ \quad (45)$$

In the above equation, the subscript “1” has been omitted to simplify the notation for the forwards reaction.

At equilibrium temperature,  $\Delta_r G^\ominus = 0$ ; thus:

$$\Delta G^+ = \Delta_{-1} G^+ \big|_{T=T_{eq}} \quad (46)$$

which, for  $T_{eq}$ , implies equality  $k_1 = k_{-1} \big|_{T=T_{eq}}$ .

Figure 2 illustrates the interpretation of Equation (45) relative to the conventional reaction path, with Figure 2b repeating Figure 2a to graphically represent Equation (35).

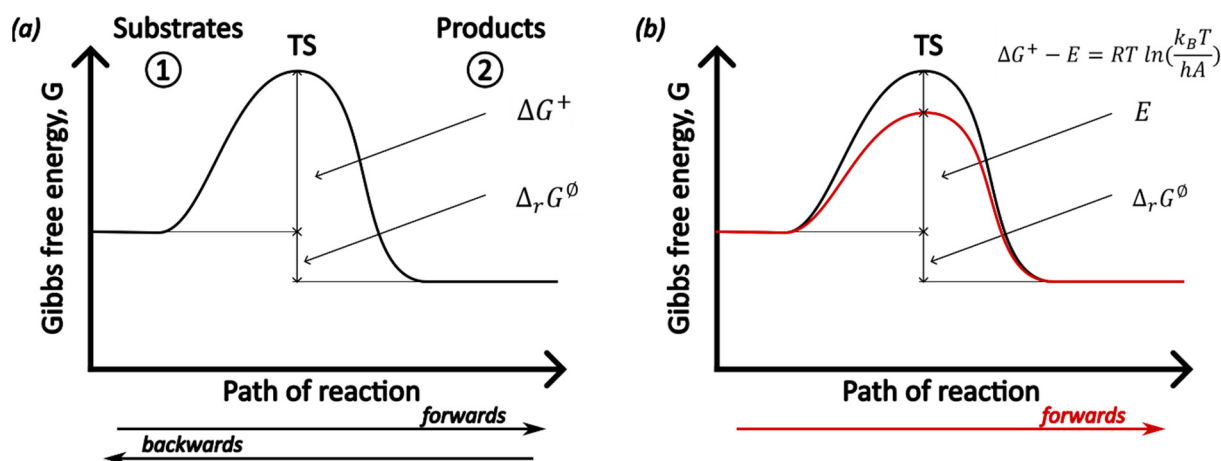


**Figure 2.** Interpretation of Equation (45) for version (a) serves to normalise the forwards–backwards reaction/process, while (b) includes only forwards, referring to the activation energy  $E$  for the forwards reaction, Equation (35).

According to Figure 2a (forwards), for TS, we can write that:

$$\Delta G^+ = G_{TS} - \sum G_S \quad (47)$$

and, similarly, for backwards:

$$\Delta_{-1} G^+ = G_{TS} - \sum G_P \quad (48)$$

By subtracting the sides of Equation (48) from Equation (47), we obtain Equation (45):

$$\Delta G^+ - \Delta_{-1}G^+ = \sum G_P - \sum G_S = \Delta_r G^\ominus \quad (49)$$

For backwards–forwards compatibility of the thermodynamic term, changing the sign is paramount:

$$\Delta_{-1}G^+ = \Delta G^+ + (-\Delta_r G^\ominus) \quad (50)$$

Equation (45), with the particular significance of the coordinate Equation (46), omits TS, and the central point is  $T_{eq}$ .

Laidler and King [55] proposed a different approach to Equation (44), namely by adding an intercept in the form of the terms  $C_1$  and  $C_{-1}$ :

$$\ln K = -\frac{\Delta_r G^\ominus}{RT}, \ln k_1 = -\frac{\Delta G^+}{RT} + C_1, \ln k_{-1} = -\frac{\Delta_{-1}G^+}{RT} + C_{-1} \quad (51)$$

and when we use Equation (51), then the notation of Equation (44) is enriched with a temperature term. Combining these, we see that:

$$\Delta_r G^\ominus = \Delta G^+ - \Delta_{-1}G^+ + RT\Delta C, \quad (52)$$

## 6.2. Approach to $\Delta_r G^\ominus$ No. 2

Equation (45) assumes that both substrates and products behave in a way that is described by phenomenological thermodynamics, or more simply, in a way that can be described by tabulated standard functions. Further relationships emerge from the considerations presented in [6]. Among other things, such relationships are able to describe the course of the nucleation of the product:

$$\Delta_r G^\ominus = \Delta G^+ - \Delta_{-1}G^+ + \Delta_n G^\ominus \quad (53)$$

Importantly, the above term  $\Delta_n G^\ominus$ , when broken down into its constituent elements, analogously leads to a description of the nucleation process in a forwards–backwards sense.

$$\Delta_n G^\ominus = RT \ln \frac{k_{-n}}{k_n} = \Delta_n G^+ - \Delta_{-n}G^+ \quad (54)$$

## 7. Balance of Free Energy of Activation in Terms of Arrhenius Rate Constant

### 7.1. Calcite Thermolysis

Graphically, the temperature profiles of the free energy are shown in Figure 3. Similar approaches for other data are presented in [4], and the detailed forms of the equations are partly taken from [4] and also [6].

The individual equations are as follows:

$$\Delta_r G^\ominus = 174.92 - 0.15T \quad (55)$$

$$\Delta G^+ = 185.55 + 0.132T, E = 191 \text{ kJ}\cdot\text{mol}^{-1} \quad (56)$$

$$\Delta_{-1}G^+ = 63.04 + 0.221T, E_{-1} = 70.56 \text{ kJ}\cdot\text{mol}^{-1} \quad (57)$$

$$\Delta_{-1}G^+ = 9.44 + 0.29T, E_{-1} = 17.52 \text{ kJ}\cdot\text{mol}^{-1} \quad (58)$$

We find that Equation (45) is satisfied for the difference of Equation (56) with (58), and then over the whole temperature range  $\Delta_n G^\ominus = 0$ .

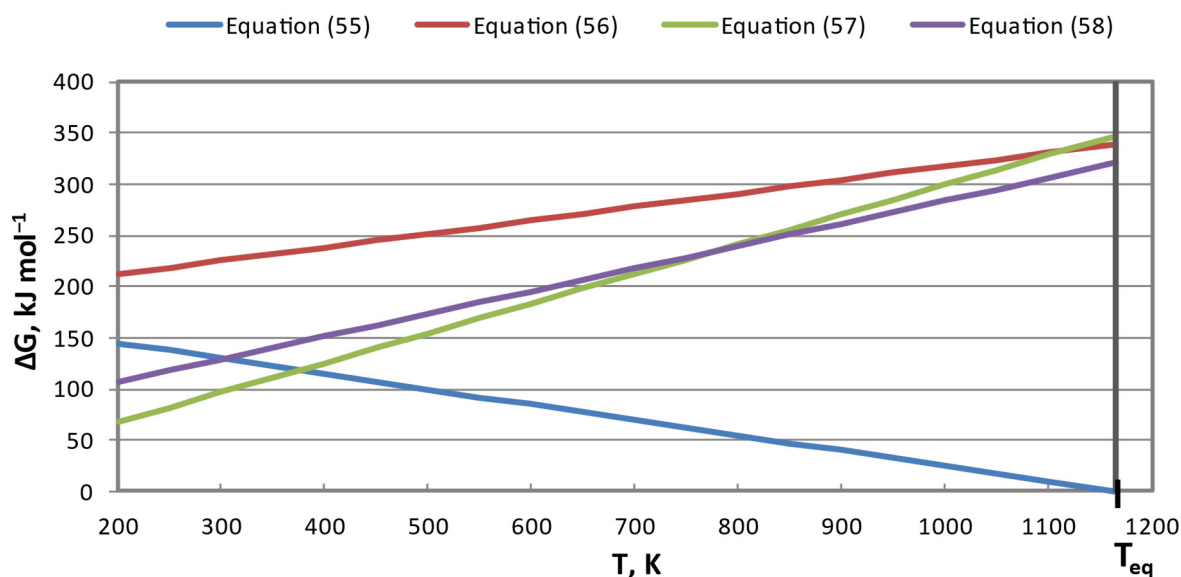


**Figure 3.** Temperature free energy profiles for calcite thermolysis,  $T_{eq} = 1166.13$  K.

Where the lines intersect, in particular thermodynamic lines with activation, e.g., Equation (55) with Equation (56) or Equations (57) and (58), the temperatures proposed in [4] can be determined and then used to calculate  $K^+$ .

$$R \ln K^+ = \Delta_r S^\ominus - \frac{\Delta_r H^\ominus}{T_K} \text{ or } R \ln K^+ = \Delta_r S^\ominus - \frac{\Delta_r H^\ominus}{T_{-K}} \quad (59)$$

From a comparison of Equations (55) and (58), we obtain  $T_{-K} = 376.09$  K, and from Equation (59), we see that  $\ln K^+ = -37.90$ , using the values of the thermodynamic functions for forwards reactions as given in Equation (55). For comparison, using Equation (41) in logarithmic form can be determined  $\ln K^+ = -38.531$  (source [6];  $E_{-1} = 17.52$  kJ·mol<sup>−1</sup>;  $\ln A = -3.238$ , where  $A$  has the unit of s<sup>−1</sup>;  $k = 1.447 \cdot 10^{-4}$  s<sup>−1</sup>). The two values of  $\ln K^+$  calculated by the two independent methods are slightly different, but they remain at a similar level of estimation. Given the imperfections of Equation (41), this is significant and, more interestingly, remains in agreement with the general approach expressed in the form of Equation (43).

The automatism resulting from the mechanical treatment of the rate constant will lead to deviations of the determined quasi-equilibrium constant  $K^+$ . This issue is discussed in [4,6,48], and in this paper, the authors illustrate the problem using Figure 1.

An important problem in considering the solid-phase thermolysis process is the balance of Equation (45) and Equations (53) and (54), which can be written in the form  $\Delta_n G^\ominus = 0$  or  $\neq 0$ .

Based on the excess free energy model  $G^E$  used in [6], the following rate constant of nucleation for calcite was proposed:

$$k_n = A_n \exp\left[-\frac{16\pi\sigma^3 V^2 N^3}{3RT(\Delta G)^2} f(\theta)\right] \quad (60)$$

The expression presented in Equation (60) is the Gibbs free energy of the formation of the critical nucleus, which, according to the classical nucleation theory, has the following form [68,69]:

$$\Delta_n G^+ = \exp\left[-\frac{16\pi\sigma^3 V^2 N^3}{3(\Delta G)^2}\right], \text{ J} \cdot \text{mol}^{-1} \quad (61)$$

Equation (61) is a component of the Turnbull–Fisher (T–F) equation (which is incompatible with the GRE). Moreover, it depends on temperature and can be both Arrhenius or non-Arrhenius [68].

For further discussion, the values of the individual components in Equation (s 60 and 61 were taken here from [50]:  $\sigma = 0.1 \text{ J}\cdot\text{m}^{-2}$  (specific surface energy),  $V = 3.64\cdot 10^{-29} \text{ m}^3$  (volume),  $N = 6.022\cdot 10^{23} \text{ mol}^{-1}$  (Avogadro number),  $f(\theta) = 0.15625$  (heterogeneous nucleation is related to the apparent contact angle  $\theta = 60^\circ$  between the embryo and the solid phase),  $\Delta G$  in  $\text{J}\cdot\text{mol}^{-1}$  (Gibbs free energy).

If one enters the data contained in [6] into Equation (60), the following equation can be written:

$$\ln k_n = \ln A_n - \frac{Z}{RT(\Delta G)^2} \quad (62)$$

Here, the individual constants mentioned above are collected in the form of a new constant  $Z = 75.75\cdot 10^{10} \text{ J}^3\cdot\text{mol}^{-3}$ . The authors in [6] also postulated a maximum nucleation rate  $k_n = A_n$ , which was reached at high temperature and high supersaturation ( $S = \frac{P_{eq}}{P}$ ). When reinterpreting, it should be noted that Equation (62) is an isoconversional view of the problem, since a variable temperature  $T$  temperature corresponds to a constant supersaturation  $S = \text{constant}$ ; however, this is difficult to explain given the current state of knowledge. In the thermolysis process for the variant with increasing temperature to  $T_{eq}$ , the partial pressure increases,  $P_i \rightarrow P_{eq}$ , and thus  $\Delta G \rightarrow 0$ , which implies  $k_n \rightarrow 0$ , and thus, the nucleation process disappears.

Following the suggestion of representing the T–F equation as a relative relation [68] and writing Equation (5) as a conversion degree function, we obtain:

$$\frac{k_n}{A_n} = \exp\left[-\frac{Z}{RT(\Delta_r H^\ominus - T\Delta_r S^\ominus + \nu_i RT \ln \alpha)^2}\right] \quad (63)$$

A graphical analysis of Equation (63) is shown in Figure 4. This graph compiles three variants of the equilibrium course of calcite thermolysis at three conversion steps, where for  $\alpha = 1$ , we observe the equilibrium  $\Delta G = \Delta_r G^\ominus$ , and  $\alpha = 0.05$  is taken as the start of the reaction progress. For the calculations, the data indicated at Equation (55) and the assumption of  $\nu_i = 1$  were used. It can be accepted that for isothermal conditions,  $T = \text{constant}$  to temperature  $T_{eq}$ , and ratio  $\frac{k_n}{A_n} \rightarrow 0$ .

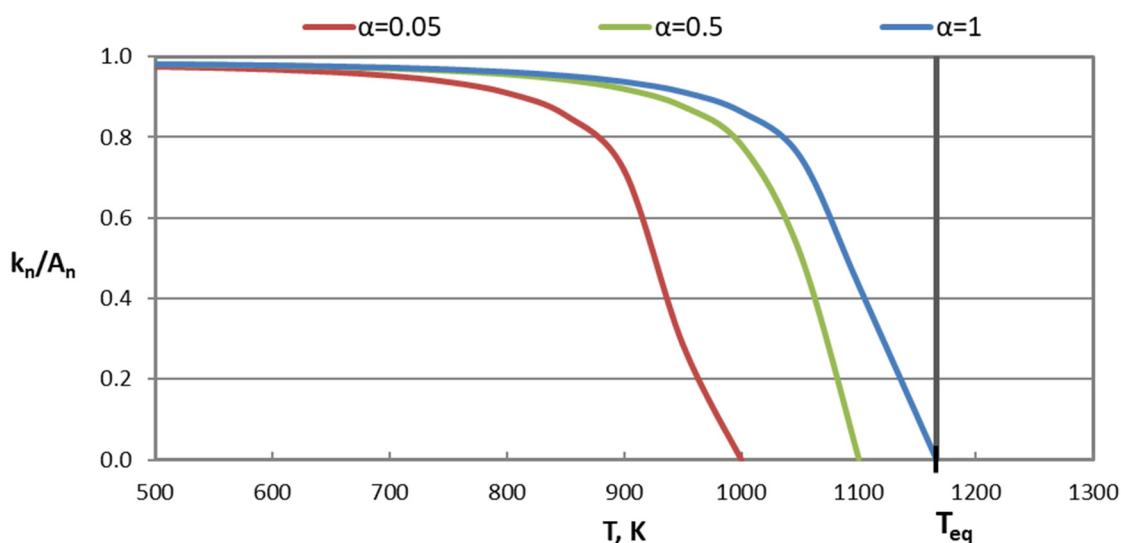


**Figure 4.** Temperature profile of relative rate constant of nucleation Equation (63), covering the range of variation for isoconversion degree ( $0.05 \leq \alpha \leq 1$ );  $T_{eq} = 1166.13 \text{ K}$ .

Again, the increase in the relative rate constant of nucleation  $> T_{eq}$ , when  $\alpha = 1$  is related to the possibility of melting and a different expression for free energy in Equation (62), for  $\text{CaO}$ ;  $T_m = 3156 \text{ K}$ ,  $\Delta H_m = 80.89 \text{ kJ}\cdot\text{mol}^{-1}$  [70]. This temperature range is not of interest for this paper. Equilibrium run refers to the case of complete decomposition of the starting substrate and equilibration of the partial pressure to atmospheric pressure. In the vicinity of the equilibrium temperature, the nucleation process can be neglected.

From the above considerations, it can be concluded that it is more convenient to analyse the model written Equation (62) by extracting the activation energy from this equation:

$$E_n = \frac{Z}{(\Delta G)^2} \quad (64)$$

For  $\Delta G = 0$ ,  $E_n \rightarrow +\infty$ , when  $\Delta G = \infty$ ,  $E_n \rightarrow 0$ , and free energy is defined by Equation (5), which covers both of the limiting cases. However, a minor remark is necessary, namely that for  $K_\alpha = 0$ ,  $\Delta G = -\infty$ , which is meaningless due to squaring. The notation according to Equation (64) may additionally include another constant, called the activation energy required for a molecule, to cross the interface separating the ordered cluster from the disordered matrix. Such a constant occurs, for example, in the T-F equation cited in [68]. Because of the model used in [6] and expressed in this work via Equation (53), the diffusion activation energies have been omitted as they are captured by Equation (54).

Of interest is the case where  $E_n = 0$ , because then the equality  $k_n = A_n$  exists. For this purpose, we analyse Equation (62) for the condition  $\frac{d \ln k_n}{dT} = 0$ , resulting in the relation, when  $|\Delta G| > 0$ :

$$\Delta G = 2T\Delta S \quad (65)$$

which, after using the classical treatment for Gibbs free energy (Equation (27)) without the activation symbol), leads to a notation that uses the special case of equality for isoconversion  $\Delta H = \Delta H^\circ$ ,  $\alpha = \text{constant}$ :

$$\Delta G = \frac{2}{3} \Delta_r H^\circ \quad (66)$$

For calcite and its standard enthalpy of thermolysis,  $\Delta_r H^\circ = 175 \cdot 10^3 \text{ J}\cdot\text{mol}^{-1}$ ,  $E_n = 55.7 \text{ J}\cdot\text{mol}^{-1}$  can be determined using Equation (64). This practically means  $E_n = 0$ , and based on above discussion on nucleation, we know that such a result is possible [69]. The range of variation in Equation (64) is  $0 \leq \Delta G \leq \Delta_r G^\circ$ , which mandates the validity of accepting the zero-activation energy. Thus, there is no need to consider the case  $|\Delta G| = \infty$ .

As follows from Equation (64), the activation energy of nucleation for  $\Delta G = 0$  reaches an infinite value, which can be considered to be completely absent when  $T = T_{eq}$ , but can still be assumed to hold when getting close to  $T_{eq}$ . To illustrate this, Figure 5 presents a comparison of the variation of nucleation activation energy as a function of temperature and conversion degree. The two plots of this relationship represent the view on to the isothermal process conditions (Figure 5a) as well as on the data obtained during thermogravimetric experimental studies that were carried out under dynamic conditions (Figure 5b) [6]. For graphical illustration, Equation (64) was used in both cases, where in place of  $\Delta G$ , the relation given by Equation (63) and the data presented in Equation (55) were applied. The rule of thumb was adopted that the nucleation process is parallel to thermolysis according to (1). To avoid exceeding  $T_{eq} = 1166.13 \text{ K}$ , the temperature range of 880–1160 K is shown on the figure only.

A comparison of these two plots leads to the conclusion that both approaches have the same common elements, e.g., a “valley” of zero energy drawn in the direction of high temperatures and conversion degree, although with markedly different slopes. What separates them are the much higher values of the activation energy of nucleation observed in the experimental data. This effect is characteristic of physical transformations, with

slower processes achieving the expected effects more easily. In the case of isotherms and the absence of synergistic interactions ( $T \cdot \ln \alpha$ ), the domain  $E_n = 0$  is much more pronounced (Figure 5a).

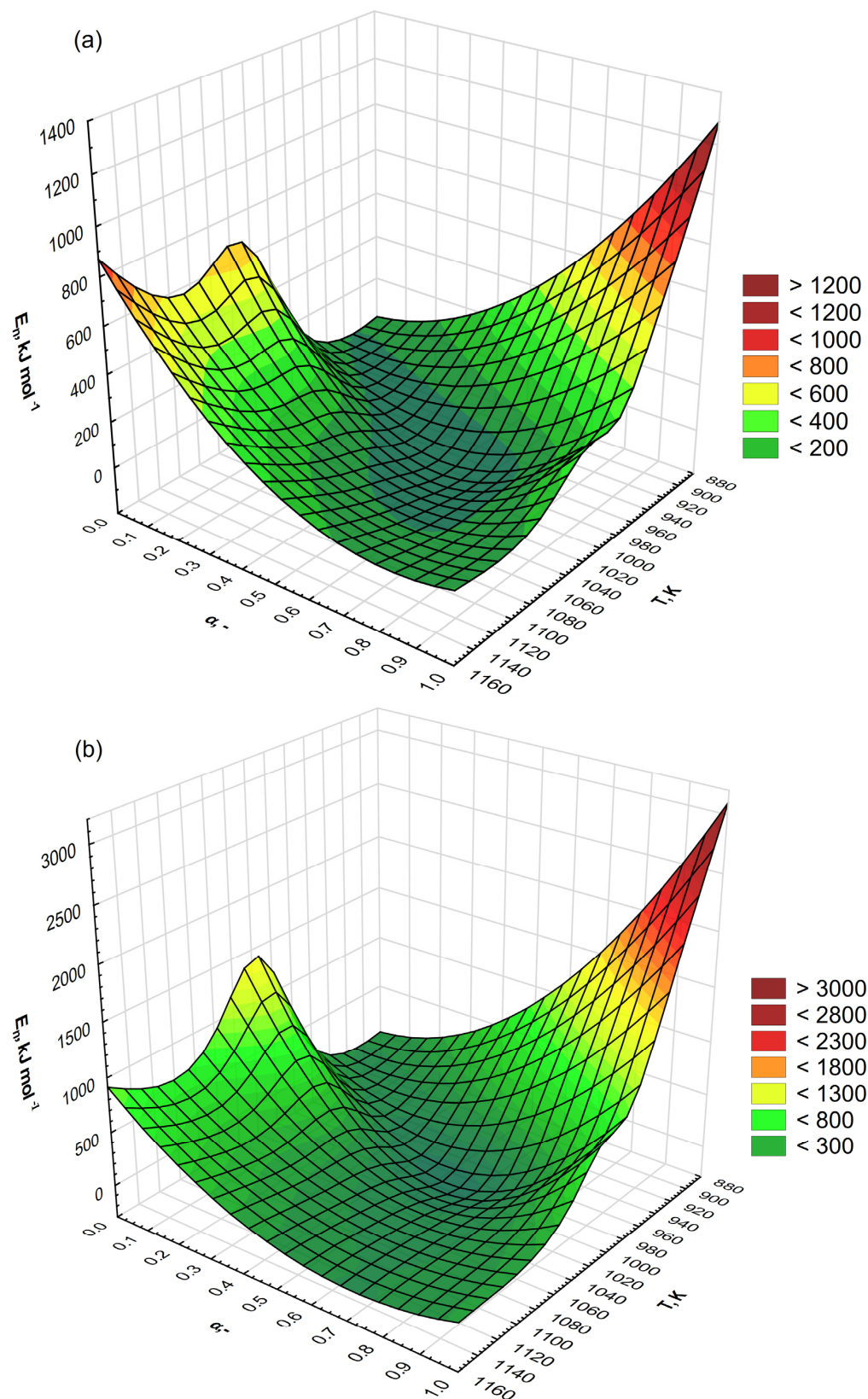


**Figure 5.** Graphical representation of the activation energy of nucleation as a parallel process during calcite thermolysis. A 3D dependence according to Equation (64):  $E_n$  vs.  $\alpha - T$ , (a) isothermal conditions, (b) experimental data under dynamic conditions of variable heating rate (data source [6]).

This interpretation leads to the conclusion that slow heating is necessary for nucleation, which leads to low process rates and this, in turn, requires a long reaction time, conversely over-accelerated reaching of high temperatures, which is achieved at high heating rates, leads to rapid deceleration of nucleation. Based on excess free energy [6], either  $G^E = 0$  and no nucleation occurs, or  $G^E > 0$ , which initiates the process. This is particularly important when using data obtained under dynamic conditions, i.e., where the heating rate  $q = \frac{dT}{dt}$  and where gas products are continuously removed from the reactor. It is important to note, however, that under dynamic conditions there is a maximum reaction rate that is not captured in the models. This imperfection is therefore a fundamental problem that needs to be addressed. The question then arises as to how to replace the isokinetic temperature  $T_{iso}$  with  $T_{max}$ , which is determined by dynamic methods.

According to the considerations presented in [3,71], for the thermolysis of the same chemical compound, the determined isokinetic temperatures vary considerably, depending on the experimental material collected and the concept for determining the kinetic parameters. Therefore, it is necessary to impose the acceptance of the KCE verified by the methods described in [31,32].

## 7.2. Methane Thermolysis

In the contrast to the thermolysis of a solid-phase substrate, the issue of the thermolysis of a gas-phase substrate presents distinct differences that require further discussion. This case is presented here using the example of a methane molecule.

Returning to the reaction/process of Equation (2), it is important to note at the outset, few fundamental thermodynamic differences exist between the two thermolysis processes. In the case of the solid phase, according to Equations (1) and (7) for  $K = 1$ ,  $\Delta_r G^\circ = 0$ , and thus  $\alpha_{eq} = 1$ , while in the case of gas-phase thermolysis for  $K = 1$ , according to Equation (17) we obtain  $\alpha_{eq} = \sqrt{\frac{K}{K+1}} = 0.4472$ . Another one can be found in the fact that with increasing temperature and dilution of methane the experimental conversion degree approaches the equilibrium value,  $\alpha \rightarrow \alpha_{eq}$ . Furthermore, it is known that the efficiency of the reaction/process of Equation (2) depends on a number of factors [5], particularly the process conditions and/or the activity of the catalyst used. With reference to the KCE and EEC effects described in [5], it can be seen that the relation  $\alpha \leq \alpha_{eq}$  is always maintained under experimental conditions, but at the same time, a distinctly different inequality  $T_{iso} > T_{eq}$  appears. Note that existing considerations on the thermolysis of solid phase suggest the opposite inequality, i.e.,  $T_{iso} < T_{eq}$  [3,19,29].

To unravel this situation, the following equation was taken as the starting point for the analysis [5]:

$$\Delta_r G^\circ = 88.04 - 0.108T, \text{ kJ}\cdot\text{mol}^{-1} \quad (67)$$

It remains in accordance with Equations (45) and (53), but let its complement be the following two free energy Equations for the activation of the reaction forwards (Equations in  $\text{kJ}\cdot\text{mol}^{-1}$ , and  $A$  in  $\text{s}^{-1}$  in the following Equation (68) data is taken from [72], while in Equation (69) from [73]):

$$\begin{aligned} \Delta G^+ &= 122.76 + 0.192 \cdot T, \\ (E &= 131.0 \text{ kJ}\cdot\text{mol}^{-1}, \ln A = 8.594) \end{aligned} \quad (68)$$

$$\begin{aligned} \Delta G^+ &= 412.46 - 0.038 \cdot T \\ (E &= 420.7 \text{ kJ}\cdot\text{mol}^{-1}, \ln A = 36.23) \end{aligned} \quad (69)$$

While for the free energy of activation for backwards, based on data from [74], we write:

$$\Delta_{-1} G^+ = 97.62 + 0.294 \cdot T$$

$$(E_{-1} = 105.9 \text{ kJ}\cdot\text{mol}^{-1}, \ln A_{-1} = -3.65) \quad (70)$$

The kinetic data for Equation (68) are for the elementary reaction realised without flow in the temperature range 700–900 °C, for pressures 2.82–5.61 MPa, and for times up to 100 s [72]. The data for Equation (68) were obtained in a perfectly mixed reactor with bypass (CPMR), where the methane flow upstream of the molten metal reaction zone is divided into two parts. The fraction bypassing the reactor is quantified as the total volumetric flow rate passing through its dead zone, and this solution is known as an used to counteract the reaction limiting factors of the hot reactor zone (1073–1323 K) [73].

The specific coefficients of Equations (67)–(70) were obtained using Equation (35), and their graphical representation is shown in Figure 6.

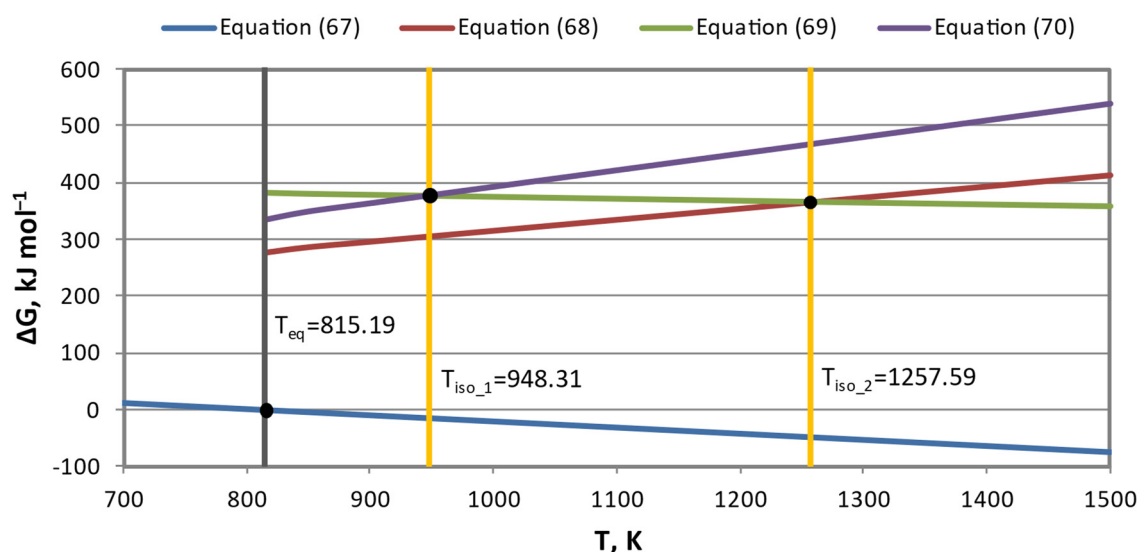


**Figure 6.** Temperature profiles of response (2) for Equations (67)–(70).

From a wide range of variation in activation energy, presented in [5] in the form of KCE, extreme cases have been selected for reactions carried out without a catalyst covering  $E = 131 - 420.7 \text{ kJ}\cdot\text{mol}^{-1}$  for the forwards. Note that these values are higher than the average enthalpy of the reaction given in Equation (67)  $\Delta_{298}H^\circ = 74.85 \text{ kJ}\cdot\text{mol}^{-1}$  [5].

It can be seen that using the following Equation as a criterion [5]:

$$E - E_{-1} = RT_{eq} \ln \frac{A}{A_{-1}} = T_{eq} \Delta S^\circ = \Delta_r H^\circ \quad (71)$$

The equivalences for the Equations (67)–(70) are not kept for every case:

- $E - E_{-1} = 122.76 - 97.62 = 25.1$  and  $E - E_{-1} = 412.46 - 97.62 = 314.8 \text{ kJ}\cdot\text{mol}^{-1}$ , (it should be,  $88.04 \text{ kJ}\cdot\text{mol}^{-1}$ )
- $\Delta_r S^\circ = R \ln \frac{A}{A_{-1}} = 8.314[8.594 - (-3.65)] = 101.8$  and  $\Delta_r S^\circ = 8.314[36.23 - (-3.65)] = 331.56 \text{ J}\cdot(\text{mol}\cdot\text{K})^{-1}$ , (it should be  $108.04 \text{ J}\cdot(\text{mol}\cdot\text{K})^{-1}$ ).

From this example, it can be seen that the experimentally determined standard entropy, which is the difference between products and substrates, indicates a much higher disorder and energy distribution than the result obtained by phenomenological thermodynamic considerations.

As already mentioned before, in contrast to the considerations presented for solid phase thermolysis reactions, where at  $\Delta_r G^\circ = 0$ ,  $K = 1$  (Equation (10), solid phase), for methane thermolysis (Equation (2), gas phase), the central point is not the equilibrium temperature ( $T_{eq} = 815.19 \text{ K}$ , from Equation (67)). Moreover according to [5], it is known

that the formation of kinetic relations approaches their isokinetic temperature  $T_{iso} > T_{eq}$ , which can be seen by comparing the forms of Equations (68) and (69). It remains interesting to note the issue of the course of the relationship given by Equation (69) in relation to the thermodynamic function described by Equation (67). Both lines have a negative slope, i.e., an increase in temperature decreases the free energy of activation, given a positive average entropy of activation,  $\Delta S^+ = 38.0 \text{ kJ} \cdot (\text{mol} \cdot \text{K})^{-1}$ , and according to Equation (47) this indicates a higher entropy in the TS state than in the entropy of the substrate (methane). An illustration of the lines shown in Figure 6 suggests that for Equations (67), (68), and (70), there is a directional correspondence of the forwards–backwards relationship. In the system of Equations (67), (69) and (70) the direction of change of Equation (69) is consistent with the direction of change of the free energy of reaction (2), which is surprising and requires further explanation.

After accepting the values given here for  $E_{-1}$  and  $\ln A_{-1}$ , the corresponding values for  $E$  and  $\ln A$  are  $193.94 \text{ kJ} \cdot \text{mol}^{-1}$  and  $9.34 (A \text{ in } \text{s}^{-1})$ , respectively. Again, note that such a coordinate is slightly different from the broad set described in [5], but the entropy agreement is close to the value determined using Equation (68). The discussion authorises a balance according to Equation (53), with a change in the index as the reference changes to carbon. Here, the additional term  $\Delta_c G^\ominus$  applies only to the structural transformations of the resulting carbon solid phase. By performing the balance, we see that:

$$\Delta_c G^\ominus = 62.9 - 0.006 \cdot T, \text{ kJ} \cdot \text{mol}^{-1} \quad (72)$$

while Equations (67), (68) and (70) result in:

$$\Delta_c G^\ominus = -226.8 + 0.224 \cdot T, \text{ kJ} \cdot \text{mol}^{-1} \quad (73)$$

In the case of Equation (72), we observed an endothermic transformation effect of the carbon structure associated with the agglomeration of amorphous forms, but the effect of temperature is small. The second case, according to Equation (73), indicates an exothermic effect associated with at least deflagration, which is an apparent effect. Setting the free energy to zero acc. to Equation (73) leads to a temperature  $T = 1012.5 \text{ K}$ . Therefore, up to this temperature, negative value decreases the free energy of activation in Equation (69), while above it, the term  $\Delta_c G^\ominus$  (note the index “c”) adapts positive values. By analogy with the considerations presented in [68], the observed high activation energy,  $E > 300 \text{ kJ} \cdot \text{mol}^{-1}$  [5,75–77], is the sum of the activation energy of the chemical reaction and physical processes, mainly related to diffusion (positive activation energy) and viscosity change (negative activation energy). This phenomenon depends on the way in which the thermolysis of methane takes place, e.g., in the molten salt/metal layer the solid phase formed “disappears” in the volume of the bed, and this greatly affects the physical phenomena that occur. Furthermore, even with ideal mixing, an increase in the activation energy is observed and its value is close to the energy of the C – H bond ( $434 \text{ kJ} \cdot \text{mol}^{-1}$ ) [5].

Excessively high activation energies in heterogeneous reactions/processes are burdened by the need to overcome effects of physical nature and so the interpretation of free energy of activation as TST can lead to incorrect conclusions. Regarding the actual methane thermolysis process, in the two cases analysed above (Equations (72) and (73)), too short reaction times for the reaction/process (2) do not lead to clear structural changes towards the formation of hexagonal graphite or even its turbostratic forms. At most, single graphite crystallites can be identified. However, it is important to note that for long reaction/process times, carbon family mixtures other than the classical allotropic carbon varieties are formed.

## 8. Discussion

According to Figure 2, the principles are first defined as the difference shown in Equation (47), and the basic formula determining the free energy of activation is expressed by equation. The analytical treatment shown in Figure 2b implies that the energy of activation is an experimental quantity and is valid for a given degree of conversion, i.e., is either fully or partially valid. The use of TST requires reference to the elementary reaction, which is not always possible in heterogeneous or complex processes. In general, the value referred to here as high activation energy has not been subjected to a specific evaluation category. For this purpose, Equation (35) has been restructured as follows:

$$\Delta G^+ = E - RT \ln A + RT \ln(BT) \quad (74)$$

The last component in Equation (74) is only temperature dependent and is universal, always the same over the assumed temperature range. For  $500 \leq T \leq 1500$  K, its linear form is represented as:

$$RT \ln(BT) = 263.04 \cdot T - 7678.7 \quad (75)$$

and by indicating the sign of the slope this can be expressed numerically in the linear form of Equation (74) written as:

$$\Delta G^+ = (E - 7678.7) - (R \ln A - 263.04) \cdot T, \text{ J} \cdot \text{mol}^{-1} \quad (76)$$

Equation (76) is a linear approximation of Equations (27), (34), (35) and (39) with respect to temperature. A recalculation of Equation (76) using the kinetic data collected in [4] leads to the linear Equation (coefficients given there and for the critical size  $\ln A = \frac{263.04}{R} = 31.638 (A \text{ in s}^{-1})$ .  $\Delta G^+$  is independent of temperature, and for  $\ln A < 31.638$ , the slope is positive, which is consistent with the considerations presented in [4–6]. Thus, the sign of the difference  $(R \ln A - 263.04) = \Delta S^+$  depends on the sign of the entropy of activation, i.e., the slope of the temperature profile of the free energy of activation. According to KCE, an increase in the activation energy increases the pre-exponential factor (and vice versa) but from a formal TST point of view, the challenge is to balance the two quantities. Furthermore these considerations explain the excessive discrepancy in the determination of the isokinetic temperature ( $T_{iso}$ ), which was presented in [5].

Equation (76) is the simplest approximation of Equation (27) and is a notation of great practical importance. Not only does it identify the basic thermodynamic activation functions, but more importantly, it also shows the importance of temperature in these considerations. In this notation, each temperature corresponds to an individual constant value of  $\Delta G^+$ , also for the isokinetic temperature ( $T_{iso}$ ), when the changing kinetic parameters satisfy KCE.

Since we are working with finite elements, using Equation (76) twice for reactions forwards and subtracting for backwards (see Equations (45) and (53)), Equation (71) leads to the following general form of a pyrolysis Equation, where the temperature term disappears:

$$\Delta_r G^\circ = E - E_{-1} - RT \ln \frac{A}{A_{-1}} + \Delta G^\circ \quad (77)$$

In addition, the non-zero value of  $\Delta G^\circ$  confirms the presence of accompanying physical phenomena.

Furthermore, a re-analysis of the elements presented in the papers [3–6] allows a comparison of aspects of TST in relation to kinetic parameters according to Arrhenius' law. A comparison between the temperature profiles of reaction/process (1) and (2) is possible on the basis of an extended free energy balance according to Equation (53). For

reaction/process (1), the analysis of the forwards and backwards paths is performed at the same level of energy states, i.e., Equation (45), and the additional term in Equation (53) is associated with the nucleation of a product. In the case of (2), it is more reasonable to complete the balance with a term describing the transformations in the resulting solid phase, i.e., in different varieties of carbon structures, thus using Equations (72) and (73). This difference in the formalisation of the task, in the case of methane thermolysis (2), significantly shifts the central point, which is the equilibrium temperature,  $T_{iso} > T_{eq}$ . It is this premise that provides the opportunity to analyse TST in the context when the temperature  $T_{eq}$  is unknown or remains difficult to determine.

Thus, Equation (76) solves the problem of converting Arrhenius kinetic parameters into free energy of activation forwards–backwards; an example for fragmentary calcite thermolysis is presented in paper [6], while other uses of this proposal are discussed below.

In the case of the thermolysis of the energetic substance 4,4'-dinitro-3,3'-diazonofuroxane [78], three decomposition steps can be identified and kinetic parameters determined. Table 1 below summarises the data given in the original paper with the calculated activation functions.

**Table 1.** Comparison of Arrhenius and TST parameters based on thermolysis of 4,4'-dinitro-3,3'-diazonofuroxane [78], determined for  $T_{iso} = 431.88$  K,  $E = \Delta H^+$  and using Equations (39) and (40).

| $E, \text{kJ} \cdot \text{mol}^{-1}$ | $\ln A, A \text{ in } s^{-1}$ | $\Delta S^+, \text{J} \cdot (\text{mol} \cdot \text{K})^{-1}$ | $\Delta G^+, \text{kJ} \cdot \text{mol}^{-1}$ |
|--------------------------------------|-------------------------------|---------------------------------------------------------------|-----------------------------------------------|
| 116.4                                | 30.6                          | 6.417                                                         | 113.63                                        |
| 147.5                                | 40.8                          | 91.220                                                        | 108.10                                        |
| 292.9                                | 80.3                          | 419.623                                                       | 111.67                                        |

From Table 1, it can be seen that the entropy of activation is positive, increases with the activation energy, and finally reaches a very high value. Interestingly, at  $T_{iso} = 431.88$  K, the calculated values of  $\Delta G^+$  are quite close to each other, reaching an average value  $111.13 \text{ kJ} \cdot \text{mol}^{-1}$ . These results are consistent with Equation (34). Some may ask, do common paths have the same end goal?

Vyazovkin's [48] recommendations for the thermolysis of biomass and the method for interpreting the results, including those obtained using the TST model, are presented in a very well-structured manner in the work [79]. The authors studied the thermolysis of peanut shells and used mathematical methods (Gaussian decomposition) to extract components such as pseudo-lignin, pseudo-cellulose, and pseudo-hemicellulose from the experimental data. A KCE analysis was then performed for each of the biomass components, to determine the isokinetic temperature. The proposal of our work was to use this temperature in the TST model instead of the maximum reaction/process rate temperature. One reason for doing so is that such a temperature was not considered during Eyring's formative years. The second and more important point is that  $T_{iso}$  is common to all heating rates.

Figure 7 is presented here to illustrate that it is not necessary to search for the maximum reaction/process rate for each heating rate. A comparison of the numerical values between the case of operating at the temperature of maximum reaction rate and the case of running the process at an isokinetic temperature leads to only slightly different values of the activation function. It is noteworthy that the latter shows both thermodynamic and kinetic justification [30].

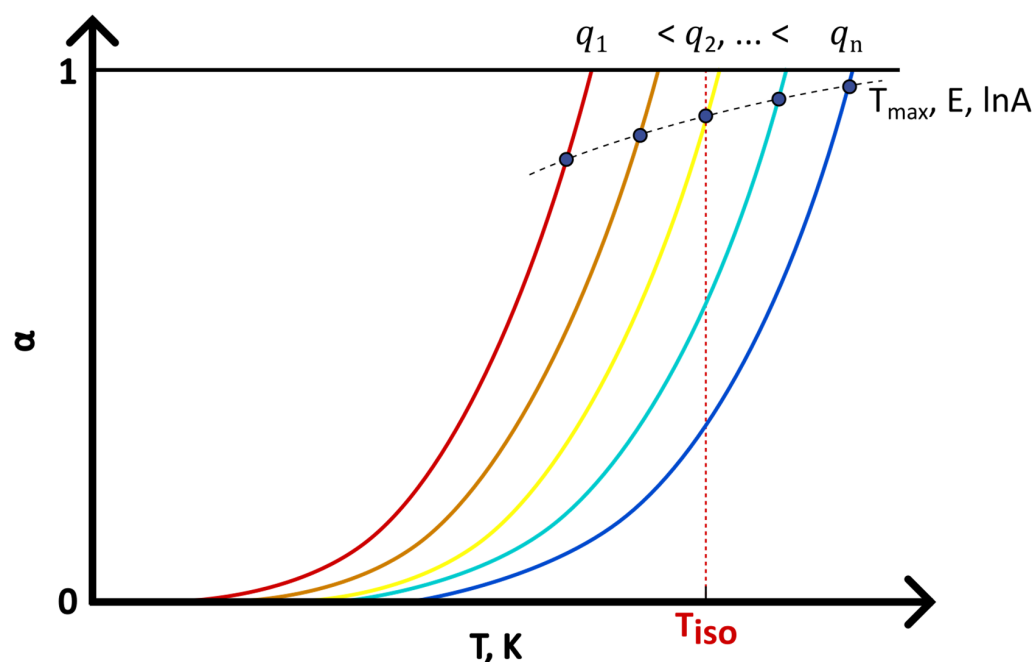


**Figure 7.** Rationale for accepting a common isokinetic temperature for a variable heating rate  $q_1$  to  $q_n$  (based on [71] for calcite). Each curve represents an example of a theoretical conversion line that has been determined for different heating rates.

This figure provides insights into the possibility of accepting the isokinetic temperature  $T_{iso}$  as the central point when the equilibrium temperature  $T_{eq}$  is not known. It should be noted that the isokinetic temperature must be verified for each individual case, since it is an experimentally determined quantity.

## 9. Conclusions

In this study, we combined the General Rate Equation with transition state theory to examine solid–gas phase thermolysis under both mass-loss (calcite decomposition) and mass-gain (methane pyrolysis) scenarios. We developed a free-energy balance that incorporates forwards and backwards activation contributions alongside a term for concurrent physical processes—such as nucleation or diffusion-viscosity changes—and derived a temperature-dependent empirical Equation (500–1500 K) linking activation parameters and  $\Delta G^\ddagger$  (Equation (76)). Our analysis employed isokinetic and equilibrium temperatures to interpret Kinetic Compensation Effects, thereby bridging Arrhenius and Eyring formulations. Despite providing a unified kinetic-thermodynamic framework, our approach was limited by the assumption of quasi-elementary reaction pathways and the exclusion of catalytic or multistep reactions. Future work should validate the model experimentally across diverse materials, extend it to non-elementary reaction networks, and explore the influence of phase-boundary phenomena and catalytic surfaces on the derived activation functions. Furthermore, the following conclusions can be drawn:

1. In order to determine thermodynamic activation functions, it has been established that the isokinetic temperature is the most reasonable for comparative purposes, both from a thermodynamic and kinetic point of view. The proof is based on deduction, as the central point for the solid phase approaches the equilibrium temperature. The experiment supports the possibility of such a substitution in the terms of mathematical formalism.
2. The suggestion made here to use  $T_{iso}$  as the central point allows TST to be used when the equilibrium temperature  $T_{eq}$  is unknown. However, this is only possible when

- analysing an elementary reaction or a separated fragments of a complex reaction pathway. Some guidance can be provided by Equation (41), which is a mathematical inversion of Eyring's concept, assuming equal kinetic rates: Arrhenius and Eyring.
3. The fundamental initial condition of TST, expressed as  $K = \frac{k_1}{k_{-1}}$  (see Equation (13)), is expanded to encompass an additional term that represents processes of a physical nature. In essence, a variation of the Gibbs free energy as a function of the reaction pathway is proposed, integrating the relationship of phenomenological thermodynamics with elements of kinetics, with activation thermodynamics serving as the unifying element (Figure 2).
  4. In the context of calcite thermolysis, the term in Equation (53) represents the nucleation of the product (CaO). It has been demonstrated that a maximum nucleation rate is guaranteed when the activation energy  $E_n \rightarrow 0$ . In the vicinity of the centre point, when  $\Delta G = 0$ , there is a pronounced increase in activation energy and an inhibition of the structural transformation process.
  5. In contrast to calcite thermolysis, in methane thermolysis, this additional term depends on the main factors in which the reaction takes place, which is ultimately expressed in terms of the activation energy characteristic of the system. The characteristics of the free energy changes of the accompanying processes, i.e., processes of a physical nature, are related to the formation of a solid phase in the form of a carbon deposit. In the context of non-catalytic reactions/processes, the observed effects can be classified as either endothermic (low E) or exothermic. The occurrence of these effects can be attributed, for instance, to the specific manner in which the reaction/process is conducted (2). The concept is illustrated by way of the bypass reactor, which is presented as a model (very high E).
  6. A general free energy of activation equation for the thermolysis reaction/process has been proposed, for the temperature range  $500 \leq T \leq 1500$  K. This equation is equivalent to that given in Equation (76), in which the activation energy is expressed in  $\text{J}\cdot\text{mol}^{-1}$  and a pre-exponential factor  $A$  in  $\text{s}^{-1}$ . In order to achieve equilibrium, Equation (77) is employed, incorporating an additional term that is intended to signify the impact of concomitant physical processes.

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## Nomenclature

|                                |                                                                                                                                                                                                      |
|--------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $A$                            | pre-exponential factor, $\text{s}^{-1}$                                                                                                                                                              |
| $b$                            | exponents                                                                                                                                                                                            |
| $B$                            | ratio of Boltzmann to Planck constant, $2.08364 \cdot 10^{10} (\text{K}\cdot\text{s})^{-1}$                                                                                                          |
| $C$                            | intercept in Equations.(51) and (52)                                                                                                                                                                 |
| $d \rightarrow 0$              | the thermodynamic limit acc. [42],                                                                                                                                                                   |
| $E$                            | activation energy, $\text{J}\cdot\text{mol}^{-1}$                                                                                                                                                    |
| $f(\alpha)$                    | kinetic function of conversion degree argument, $\alpha$                                                                                                                                             |
| $\Delta G, \Delta H, \Delta S$ | thermodynamic functions; accordingly free energy $\text{J}\cdot\text{mol}^{-1}$ , enthalpy $\text{J}\cdot\text{mol}^{-1}$ , and entropy $\text{J}\cdot(\text{mol}\cdot\text{K})^{-1}$ , respectively |

|                             |                                                                                                                  |
|-----------------------------|------------------------------------------------------------------------------------------------------------------|
| $G^E$                       | excess free energy, J                                                                                            |
| $h$                         | Planck constant, $6.62607 \cdot 10^{-34}$ J·s                                                                    |
| $k, k(T)$                   | rate constant, $s^{-1}$                                                                                          |
| $k_B$                       | Boltzmann constant, $1.38065 \cdot 10^{-24}$ J·K $^{-1}$                                                         |
| $K$                         | equilibrium constant                                                                                             |
| $n$                         | molecularity of the reaction, $n = 0, 1$ or $2$                                                                  |
| $N$                         | Avogadro constant, $6.022 \cdot 10^{23}$ mol $^{-1}$                                                             |
| $P$                         | pressure, Pa                                                                                                     |
| $P_i$                       | partial pressure, Pa                                                                                             |
| $R$                         | universal gas constant, $8.314$ J·(mol·K) $^{-1}$ ,                                                              |
| $q$                         | heating rate, K·min $^{-1}$ ,                                                                                    |
| $r$                         | reaction rate, $s^{-1}$ ,                                                                                        |
| $S$                         | supersaturation, $1 \leq S < \infty$                                                                             |
| $t$                         | time, $s^{-1}$                                                                                                   |
| $t_v$                       | lifetime of transition-state acc. [60]                                                                           |
| $T$                         | absolute temperature, K                                                                                          |
| $V$                         | volume, m $^3$                                                                                                   |
| $x$                         | mol fraction, $0 \leq x \leq 1$ ,                                                                                |
| $Z$                         | constant, $75.75 \cdot 10^{10}$ J $^3$ ·mol $^{-3}$ , Equations (62)–(64)                                        |
| $\alpha$                    | conversion degree, $0 < \alpha \leq 1$                                                                           |
| $\nu$                       | vibrational and/or oscillation frequency, $s^{-1}$ , (in [60] $\nu$ is defined as decomposition frequency of TS) |
| $\nu_i$                     | stoichiometric ratio                                                                                             |
| $\sigma$                    | specific surface energy, J·m $^{-2}$ ,                                                                           |
| $\varepsilon \rightarrow E$ | when $d \rightarrow 0$ acc. [39]                                                                                 |
| $\chi$                      | transmission coefficient in Equations (22), (26) and (28), assumed $\chi = 1$                                    |
| $\theta$                    | apparent contact angle between the embryophase and the solid phase, °                                            |
| Subscripts                  |                                                                                                                  |
| 1, $-1$ acc. to             | forwards, backwards                                                                                              |
| 1, 2, n                     | refers to Figure 7                                                                                               |
| c                           | refers to carbon                                                                                                 |
| eq                          | equilibrium                                                                                                      |
| exp                         | experiment                                                                                                       |
| hm                          | refers to harmonic mean                                                                                          |
| iso                         | isokinetic                                                                                                       |
| $K$                         | equilibrium for forwards                                                                                         |
| $(-K)$                      | equilibrium for backwards                                                                                        |
| $m$                         | melting temperature                                                                                              |
| max                         | maximum of rate reaction/process                                                                                 |
| $n$                         | nucleation                                                                                                       |
| $(-n)$                      | nucleation inhibition                                                                                            |
| $r$                         | reaction                                                                                                         |
| $P$                         | products                                                                                                         |
| $S$                         | substrates                                                                                                       |
| TS                          | transition state                                                                                                 |
| TST                         | transition state theory                                                                                          |
| $\alpha$                    | refers to conversion degree                                                                                      |
| Superscripts                |                                                                                                                  |
| +                           | thermodynamic activation functions                                                                               |
| $\emptyset$                 | standard condition                                                                                               |

## Abbreviations

CPMR—perfectly mixed reactor with bypass, CRTA—Controlled Transformation Rate Thermal Analysis, DFE—Distance from Equilibrium or far from equilibrium, EEC—Enthalpy–Entropy–Compensation, GRE—General Rate Equation, KCE—Kinetic Compensation Effect, T–F—Turnbull–Fisher Equation, TS—transition state, TST—transition state theory.

## Appendix A

Differentiating the expression in Equation (14) as a function of temperature, we see that:

$$\frac{dx}{dt} = -\frac{2}{(1+\alpha)^2} \cdot \frac{d\alpha}{dt} \quad (\text{A1})$$

and by substituting the Equations (A1), (13) and (14) into Equation (12) after rearranging, we obtain

$$\frac{d\alpha}{dt} = \frac{k_1}{2} (1 - \alpha^2) \left[ 1 - \frac{4\alpha^2}{(1 - \alpha^2) \cdot K} \right] \quad (\text{A2})$$

According to Equation (17), the term (A2) can also be expressed as Equation (16).

After multiplication, Equation (A2) can be expressed as

$$\frac{d\alpha}{dt} = \frac{k_1}{2} \left( 1 - \alpha^2 - \frac{4\alpha^2}{K} \right) \quad (\text{A3})$$

and in Equation (A3) the equilibrium constant is given in the algebraic form of Equation (17), which leads to

$$\frac{d\alpha}{dt} = \frac{k_1}{2} \left[ 1 - \alpha^2 - \frac{(1 - \alpha_{eq}^2)\alpha^2}{\alpha_{eq}^2} \right] \quad (\text{A4})$$

which, after calculation, finally yields Equation (15).

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