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Introducing an Approach to Effective Mass of Activated Complex

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Additional information is available at the end of the chapter

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Abstract

This chapter provides the information about the concept of effective mass and effective velocity of the activated complex and its connection to the transition state theory. Therefore, these parameters are of essential importance for the field of homogenous as well as heterogeneous kinetics. They also prove to be useful for the calculation of many other properties of activated state, such as momentum, energetic density, mass flux, etc., as will be demonstrated on the example of thermal decomposition of calcite and aragonite. Since the activation energy and the momentum of activated state enable to complete the characterization of motion of this instanton (pseudoparticle) alongside the reaction coordinate, these parameters can be then considered as two quantum numbers of activated complex. The quantum numbers of activated state, that is, the activation energy and momentum, also explain the relation of activated complex to Planck energy, length and time, as well as to the Gravitational constant. This idea was also applied to derive the wave function of activated complex pseudoparticle, which is affected by the isotopic composition of the sample and polymorphism as well. Furthermore, the findings introduced in this chapter enable to derive and propose the modified Kissinger equation and experimental solution for the approximation parameter in the Doyle equation of temperature integral.

Keywords: activated complex, activated state, effective mass, effective velocity, mean lifetime, half-life, group velocity, phase velocity, momentum, kinetics, transition state theory, activation energy, quantum numbers, Schrödinger equation, instanton, pseudoparticle, wave function, modified Kissinger equation, temperature integral, approximation parameter, thermal decomposition of solids

1. Chapter introduction and basic assumptions

“Transition state theory has a long history and bright future” — Truhlar et al [1].

The definition of effective or reduced mass of activated complex ($M^\#$) is one of the basic assumptions of new kinetic approach to the calculation of activation energy, which was suggested and described in previous work in detail [2]. In its simplest form, the formula of this approach can be written as follows:

$$E_a = \text{const.}'' T_{m,\Theta}^2 M^\# = (\text{const.}''' T_{m,\Theta})^2 M^\# = RT_{m,\Theta}^2 \frac{\partial \ln Q^\#}{\partial T} \quad (1)$$

where $T_{m,\Theta}$ is the thermodynamic (absolute Kelvin scale) temperature of peak measured by thermal analysis (TA [3–7], such as DTA¹, DTG², DSC³...) with the heating rate (Θ) of 1 K·min⁻¹ or extrapolated to this heating rate (please refer to Eq. 12 and **Figure 2(b)**), $Q^\#$ is the partition function of activated molecule (please refer to discussion of Eq. 24 and Eqs. 8 and 14 in Chapter 2), and:

$$\begin{aligned} \text{const.}'' &= \frac{R}{M^\#} \frac{\partial \ln Q^\#}{\partial T} = \frac{k_B}{m_{(1)}^\#} \frac{\partial \ln Q^\#}{\partial T} = \text{const.}'''^2 \\ &\approx \text{csch}(e) + 1 = 1 + \frac{1}{\sinh(e)} = 1 + \frac{2}{e^e - e^{-e}} = 1.1326\dots \end{aligned} \quad (2)$$

is the square of temperature-rate kinetic coefficient⁴ ($\text{const.}''' = 1.0642\dots \text{ m}\cdot\text{K}^{-1}\cdot\text{s}^{-1}$)⁵, which can be e.g. also represented by the following series:

$$\text{const.}'' \approx 1 + 2e^{-e} \sum_{k=0}^{\infty} e^{-2ek} \quad (3)$$

where $m_{(1)}^\# = M^\# / N_A$ is the mass of activated molecule and the constant $e = 2.71828\dots$ is the base of natural logarithms, that is the Euler's number⁶, which is also known as the Napier's

¹Differential thermal analysis (DTA) is the TA method where the difference between heat flow rates into a sample and inert reference material (usually alumina) is measured [3]. The calibration of DTA and DSC³ instruments uses melting and phase transition of temperature standard reference materials such as pure metals (In, Sn, Zn, Ag, Au...) or salts KNO₃, KClO₄, Ag₂SO₄, K₂CrO₄, quartz, K₂SO₄, BaCO₃ and SrCO₃. A comprehensive effort related to standardization and nomenclature of TA methods was launched in 1965 by the International Confederation for Thermal Analysis (ICTA) [4, 6]. In 1992, the name was changed to International Confederation for Thermal Analysis and Calorimetry (ICTAC) in order to reflect close relationship between TA and calorimetry.

²DTG, where adjective derivative "D" is pertaining 1st derivative (mathematical) of TG (thermogravimetric) or TGA (Thermogravimetric Analysis) curve (thermoanalytical or ICTAC discouraged collocation thermal curve) [3].

³Differential scanning calorimetry (DSC) is the TA method where the heat flow rate difference between sample and reference material is measured [3].

⁴The numerical value of $\text{const.}''$ to 20 decimal places is 1.13255326439210664113... The decimal approximation for const. (Eq.2) is then 1.06421485818988011399...

⁵In order to avoid the confusion with the rate constant of reaction, this work uses the abbreviation " $\text{const.}''$ ", instead of letter " k ".

constant⁷. This infinite sum will converge very rapidly. The value of *const.* is reached even for the first two members of this series.

More general expression for Eq. 1 is given by the following formula:

$$E_a \Theta^{\frac{(2-d)RT_{m,\Theta 1}}{E_a}} = \text{const.} T_{m,\Theta}^2 M^\# \quad (4)$$

where $d = \ln(T_{m,\Theta \neq 1}/T_{m,\Theta 1}) / \ln \Theta$ is the constant exponent (power) of power function (please refer to Eq. 12) with the scaling factor $T_{m,\Theta 1}$:

$$T_{m,\Theta} = T_{m,\Theta 1} \Theta^d \Rightarrow \Theta = \left(\frac{T_{m,\Theta}}{T_{m,\Theta 1}} \right)^{\frac{1}{d}} \quad (5)$$

Since the value of power in Eq. 5 is $d \ll 1$, the relation 4 can also be written in the following form [2]:

$$E_a \Theta^{\frac{2RT_{m,\Theta 1}}{E_a}} \approx \text{const.} T_{m,\Theta}^2 M^\# \quad (6)$$

For example, the DTG peak (numerical derivation of thermogravimetric experiment) for the thermal decomposition of calcite (Eq. 33 in Chapter 2) heated with the rate of 1 K·min⁻¹ under inert atmosphere of nitrogen is shown in **Figure 1**.

Since the activation energy of this reaction (Eq. 33 in Chapter 2) is already known (please refer to **Figure 2(a)** in Chapter 2), it is possible to calculate the mechanism of the process using the formula⁸ of Augis and Bennett [8]:

⁷The constant (irrational transcendental number) was actually discovered by the Swiss mathematician Jacob Bernoulli (1655–1684), who solved (1683) the value of the formula:

$$\lim_{n \rightarrow \infty} \left(1 + \frac{1}{n} \right)^n = e. \quad (a)$$

Bernoulli is the most known for the solution (1696) of the Bernoulli differential equation:

$$y' + P(x)y = Q(x)y^n; \quad (b)$$

where n can be any real number (R) but $n \neq 0$ and 1.

⁸With the exception of possible change in the reaction mechanism of the process, which may take place with increasing temperature (please refer to discussion of **Figure 10**), the value of kinetic coefficient should stay constant over the given interval of temperature (please refer to Footnote 9). Within the same interval it should be also insensitive to the shift of peak temperature with heating rate (Eqs.8 and 12). In the case that the average value of FWHM over the investigated interval of heating rate is applied for the calculation of kinetic exponent, the obtained dependence can be accurately approximated by the power law. Despite of the fact, that coefficient of variation is usually lower than 10%, the non-zero value of skewness and kurtosis of data means that results are not normally distributed. Therefore, the calculation of kinetic exponent with the average value of FWHM over the investigated interval of heating rate cannot be recommended.

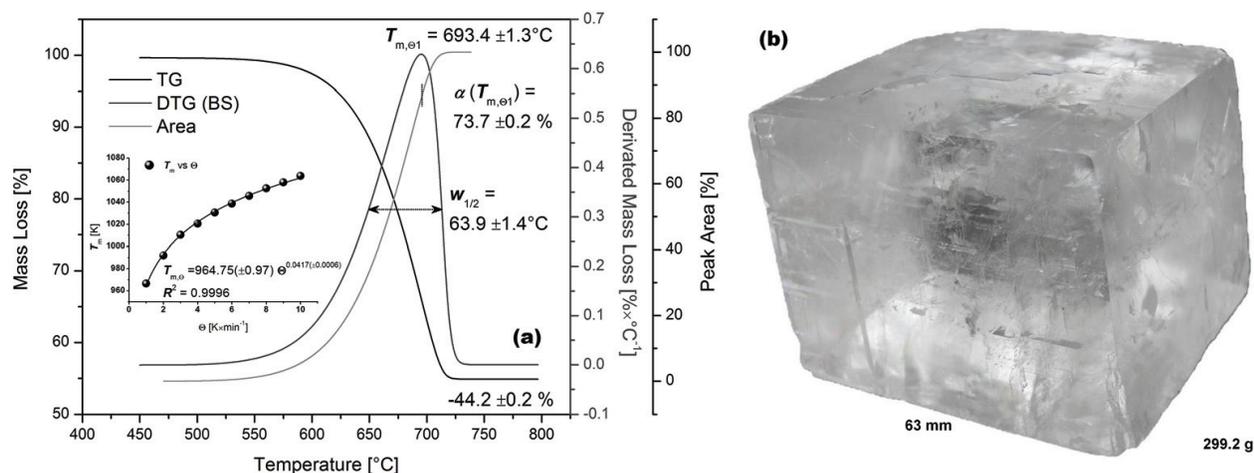


Figure 1. Thermal decomposition of calcite (20 mg) heated with the rate of $1 \text{ K}\cdot\text{min}^{-1}$ under inert (N_2) atmosphere (a) (Since the kinetics of the process was evaluated from DTG only, the thermogram (DTA curve) is not plotted in this graph.). DTG peak was subtracted to baseline (BS). The plot of T_m vs. Θ is shown in detail. The photograph (photography from author's mineralogical collection) of analyzed calcite specimen in the variety of well-developed transparent rhomb of Iceland spar (b).

$$n = \frac{2.5 RT_m^2}{w_{1/2} E_a} \quad (7)$$

where R is the universal gas constant ($8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$), n is a dimensionless exponent of Avrami equation (kinetic coefficient)⁹ [9–12], which is related to the mechanism of the process also known as the kinetic exponent) and $w_{1/2}$ is the full width at half maximum of peak (FWHM). According to Christian [13], this particular value of $n = 1.64$ corresponds to the zero or decreasing nucleation rate where the growth of new phase is controlled by the diffusion.

Before we continue, it is also interesting to solve the nature of apparent change of kinetic coefficient with heating rate. This behavior results from the effect of heating rate on the peak temperature and full width at half maximum of peak (Eq. 7), while the value of activation energy stays constant (please check this assumption with regard to the discussion of Eqs. 19–24 in Chapter 1 and Footnote 44). Both dependencies can be accurately approximated by the power law:

⁹Together with the activation energy and the frequency factor, the kinetic coefficient is the part of so-called kinetic triplet. There is no clear physical interpretation for this constant (n , reaction "order", nucleation rate, growth morphology, etc.), as well as for so-called effective overall reaction rate constant or temperature-dependent factor (k , which depends on the nucleation as well as on the growth rate) in the Avrami equation:

$$\alpha = 1 - \exp(-[kt]^n);$$

where t is the time and α is the degree of conversion (fractional conversion, formed (crystallized) volume fraction). The Arrhenius type of equation (Eq. 7 in Chapter 1) is usually assumed for the temperature dependence of $k(T)$. It should also be pointed out that the equation was independently developed several times. Therefore, it is also known as the Johnson and Mehl [12] - Avrami [9, 10] - Kolmogorov [11] (KJMA) equation.

$$T_{m,\Theta}^2 = T_{m,\Theta 1}^2 \Theta^a = \frac{n w_{1/2,\Theta 1} E_a}{2.5 R} \Theta^a \quad (8)$$

and:

$$w_{1/2,\Theta} = w_{1/2,\Theta 1} \Theta^b = \frac{2.5 R}{n \text{const.} M^\#} \Theta^b = \frac{18.352}{n M^\#} \Theta^b. \quad (9)$$

where $T_{m,\Theta 1}^2$ and $w_{1/2,\Theta 1}$ are the scale factors (coefficients) and a and b are the scaling exponents for argument Θ , respectively.

With regard to introducing the approach to the compensation of the effect of heating rate on calculated value of kinetic exponent, Eqs. 7–9 can be combined and further treated as follows:

$$n = \frac{2.5 R T_{m,\Theta 1}^2}{w_{1/2,\Theta 1} E_a} = \frac{2.5 R T_{m,\Theta}^2}{w_{1/2,\Theta} E_a} \Theta^{b-a} \quad (10)$$

where the kinetic coefficient, the fraction $(2.5 R T_{m,\Theta}^2 / w_{1/2,\Theta} E_a)$ as well as the correction term Θ^{b-a} are all dimensionless and $T_{m,\Theta 1}^2 / T_{m,\Theta}^2 = (w_{1/2,\Theta 1} / w_{1/2,\Theta}) \Theta^{b-a}$. It can also be derived, that the activation energy is:

$$E_a = \frac{2.5 R T_{m,\Theta 1}^2}{w_{1/2,\Theta 1} n} = \frac{2.5 R T_{m,\Theta}^2}{w_{1/2,\Theta} n} \Theta^{a-b}. \quad (11)$$

Using the experimental data for the abovementioned example of the process of thermal decomposition of calcite, the dependence of $T_{m,\Theta}^2$, $w_{1/2,\Theta}$ and Θ^{b-a} on heating rate is shown in **Figure 2(a)**.

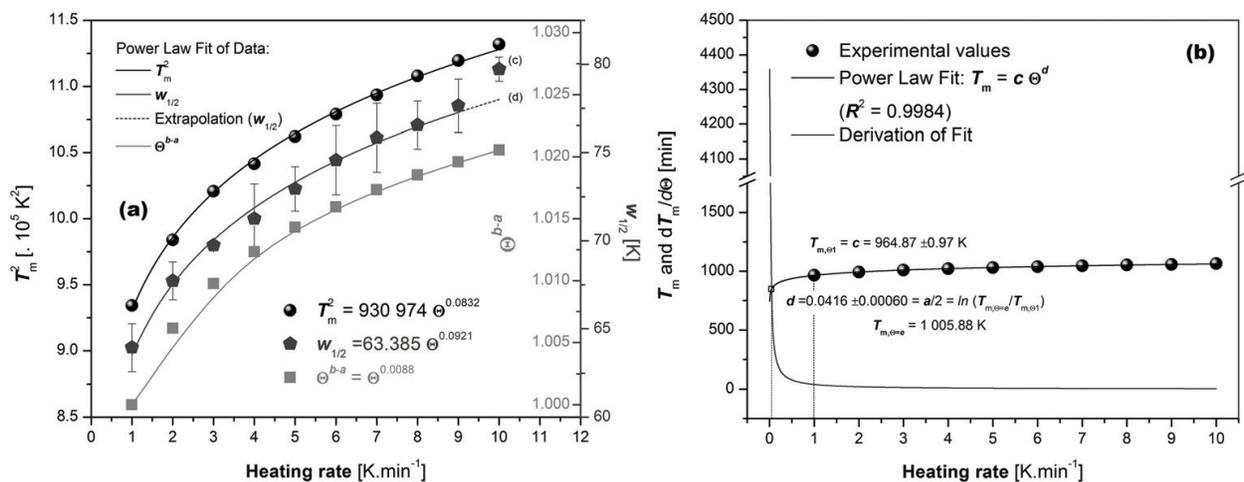


Figure 2. Change of $T_{m,\Theta}^2$, $w_{1/2}$ and Θ^{b-a} with heating rate (a) and dependence of peak temperature on heating rate (b). Excluding the last outlying value (c), the fit was extrapolated to the heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ (d).

It is obvious that the power dependence of the peak temperature (T_m) on heating rate (Θ), please refer also to previous work [2]) is:

$$T_{m,\Theta} = c \Theta^d = T_{m,\Theta 1} \Theta^{\frac{a}{2}} \quad (12)$$

where $c = T_{m,\Theta 1}$ (Eq. 5). In contrast to the scale factor, the nature of scale coefficient d is much more puzzling. The first derivation of Eq. 12 according to the heating rate gives an equation:

$$\frac{\partial T_{m,\Theta}}{\partial \Theta} = cd \Theta^{d-1} = T_{m,\Theta 1} \ln \left(\frac{T_{m,\Theta=e}}{T_{m,\Theta 1}} \right) \Theta^{\frac{a}{2}-1}. \quad (13)$$

Figure 2(b) shows the function (Eq. 12) and its derivation (Eq. 13) with the intersection point for $\Theta = d$ ¹⁰. It can also be written that:

$$d = \ln \left(\frac{T_{m,\Theta=e}}{c} \right) / \ln(e) = \ln \left(\frac{T_{m,\Theta=e}}{T_{m,\Theta 1}} \right) = a - \ln \left(\frac{T_{m,\Theta=e}}{T_{m,\Theta 1}} \right) = \frac{a}{2} \quad (14)$$

where $T_{m,\Theta=e}$ is the peak temperature calculated (Eq. 12) for the heating rate equal to the Euler number.

Since the formula obtained by the first derivation of Eq. 9 according to the heating rate is analogical to Eq. 13:

$$\frac{\partial w_{1/2,\Theta}}{\partial \Theta} = bw_{1/2,\Theta 1} \Theta^{b-1} \quad (15)$$

it can be treated with similar manner. Analogically to Eq. 14, it can be written:

$$b = \ln \left(\frac{w_{1/2,\Theta=e}}{w_{1/2,\Theta 1}} \right). \quad (16)$$

Eqs. 8, 12, 14 and 17 then provide the set of important parameters, which can have interesting utilization in many branches of heterogeneous kinetics. For example, it enables to eliminate the constant term from Kissinger Equation [14, 15]:

$$\ln \left(\frac{\Theta}{T_m^2} \right) = -\frac{E_a}{RT_m} + C. \quad (17)$$

The formulation of C for $\Theta = 1$ and $e = (T_{m,\Theta=e}/T_{m,\Theta 1})^{1/d^\circ} C \cdot \text{min}^{-1}$ (Eqs. 5 and 12) enables to write the following relations:

¹⁰The ratio of derivation (Eq. 13) to its function (Eq. 12) is:

$$\frac{cd \Theta^{d-1}}{c \Theta^d} = \frac{d}{\Theta} \quad (a)$$

so $d/\Theta = 1$ if $d = \Theta$.

$$\ln\left(\frac{1}{T_{m,\Theta 1}^2}\right) = -\frac{E_a}{RT_{m,\Theta 1}} + C \Rightarrow C = \frac{E_a}{RT_{m,\Theta 1}} - \ln\left(T_{m,\Theta 1}^2\right) \quad [\Theta = 1]$$

$$1 - \ln\left(T_{m,\Theta=e}^2\right) = -\frac{E_a}{RT_{m,\Theta=e}} + C \Rightarrow C = \frac{E_a}{RT_{m,\Theta=e}} - \ln\left(T_{m,\Theta=e}^2\right) + 1 \quad [\Theta = e]$$
(18)

The substitution from Eqs. (8) and (18) to Eq. 17 then leads to the following relation for the effective mass of activated complex¹¹:

¹¹It is then possible to write the relation:

$$\frac{E_a}{RT_{m,\Theta 1}} - 2 \ln T_{m,\Theta 1} = \frac{E_a}{RT_{m,\Theta=e}} - 2 \ln T_{m,\Theta=e} + 1$$
(a)

which can be further treated as follows:

$$\ln \frac{T_{m,\Theta=e}^2}{T_{m,\Theta 1}^2} = a \ln e = a = \frac{E_a}{R} \left(\frac{1}{T_{m,\Theta=e}} - \frac{1}{T_{m,\Theta 1}} \right) + 1.$$
(b)

The combination of (b) with Eq. 1 and further treatment leads to the relation:

$$E_a = \text{const.} \cdot T_{m,\Theta 1}^2 M^\# = \frac{R(a-1)}{\frac{1}{T_{m,\Theta=e}} - \frac{1}{T_{m,\Theta 1}}} \Rightarrow M^\# = \frac{R(a-1)}{\text{const.} \cdot \left(\frac{T_{m,\Theta 1}^2}{T_{m,\Theta=e}} - T_{m,\Theta 1} \right)}.$$
(c)

Using the general solution of Eq. 18:

$$C = \frac{1}{a} \ln \left(\frac{T_{m,\Theta}^2}{T_{m,\Theta 1}^2} \right) - \ln T_{m,\Theta}^2 + \frac{E_a}{RT_{m,\Theta}}.$$
(d)

A modified Kissinger equation can be derived:

$$\frac{2(a-1) \ln \frac{T_{m,\Theta 1}}{T_{m,\Theta}}}{a} = (1-a) \ln \Theta = -\frac{E_a}{R} \left(\frac{1}{T_{m,\Theta}} - \frac{1}{T_{m,\Theta 1}} \right);$$
(e)

where the plot of $(1-a) \ln \Theta$ versus $(1/T_{m,\Theta} - 1/T_{m,\Theta 1})$ is the straight line with the slope (gradient) of $-E_a/R$ (please refer also to Eqs. 8 and 14). The value of C can be then calculated from Eq.18 or Eq. (d).

It is also obvious that:

$$\frac{T_{m,\Theta=e}^2}{T_{m,\Theta 1}^2} = e^a \Rightarrow \frac{T_{m,\Theta=e}}{T_{m,\Theta 1}} = \sqrt{e^a} = e^{a/2} \text{ and } \ln \left(\frac{T_{m,\Theta=e}^2}{T_{m,\Theta 1}^2} \right) = a.$$
(f)

That means that the dependence of peak temperature on the heating rate (Eq. 8) can be ascertained from only two measurements carried out with the heating rate $\Theta = 1$ and e (please refer to the Footnote 7). The same data can also be used for direct calculation of effective mass of activated complex (Eq. 19) and then for the activation energy (Eq. 1). The frequency factor can then be directly calculated as follows:

$$A = \frac{2.5 \exp\left(\frac{E_a}{RT_{m,\Theta 1}}\right)}{60 w_{1/2,\Theta 1}};$$
(g)

where the denominator expresses the peak's FWHM ($60 w_{1/2,\Theta 1} / \Theta [s^{-1}]$) measured with the heating rate $\Theta = 1 K \cdot min^{-1}$, while the numerator is dimensionless (please refer also to Eq. 54). Since the kinetic exponent can be calculated from Eq. 7, whole kinetic triplet (please refer to Footnote 9) can be determined by this method.

$$M^{\#} = \frac{R \left(\ln \frac{T_{m, \Theta=e}^2}{T_{m, \Theta 1}^2} - 1 \right)}{\text{const.}'' \left(\frac{T_{m, \Theta 1}^2}{T_{m, \Theta=e}} - T_{m, \Theta 1} \right)} = \frac{R (a - 1)}{\text{const.}'' \left(\frac{T_{m, \Theta 1}^2}{T_{m, \Theta=e}} - T_{m, \Theta 1} \right)}. \quad (19)$$

This relation provides an easy experimental way for the determination of effective mass of activated complex from only two TA¹ experiments. Furthermore, the modified Kissinger equation can be derived by similar way (please refer to Eq. (e) in Footnote 11).

Another example is the application of Eq. 16 in the experimental solution of approximation parameter $B(x)$ in the empirical Doyle equation for temperature integral $p(x)$ [16]:

$$p(x) = 7.03 \cdot 10^{-3} \exp(xB(x)) \quad (20)$$

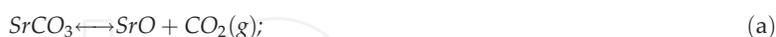
in the following form¹²:

$$p(x) = 7.03 \cdot 10^{-3} \exp \left(x \frac{T_{m, \Theta=e}}{T_{m, \Theta 1}} \right) = 7.03 \cdot 10^{-3} \exp(x \sqrt{e^a}) \quad (21)$$

where the quantity of $x = E_a/RT$. The published value for the term $B(x)$ ranges from 1.195 to 1.034 with the average value of 1.052 [17, 18]. Suggested Eq. 21 then provides a reasonable experimental solution for the parameter $B(x)$ in particular reaction system, for example, $B(x) = 1.043$ for the process of thermal decomposition of calcite¹³.

¹²In further work, we dealt with the most important formulation of modified equation, where the approach of compensation of the mutual influence between the transport of heat and the transport of mass was applied.

¹³The processes of thermal decomposition of calcite (**Figure 1**) and aragonite (**Figure 11**) show $B(x) = 1.043$ and 1.040 (please refer also to the footnote 51). When using the experimental data from previous work focused on the kinetics of thermal decomposition of strontium carbonate [39]:



the value of $B(x)$ is 1.036 for α -(orthorhombic) and 1.045 for β -SrCO₃ (hexagonal) polymorph. Presently studied process of thermal decomposition of barium carbonate:

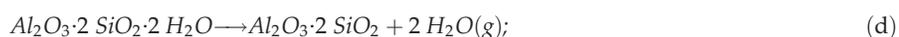


$B(x) = 1.003$. Therefore, the value of $B(x)$ decreases in the following order:



that is, with increasing relative atomic mass of Alkaline Earth Element (AEE) atom, and the value is also lower for high-temperature (hexagonal) phase than for low-temperature polymorph of carbonate. It was also recognized that the value of $B(x)$ is not affected by the size of crystallites in the sample.

Another example could be the dehydroxylation step during the process of thermal decomposition (400–700°C) of kaolinite [15]:



In which the parameter $B(x) = 1.031$.

Since the average value of $B(x)$ is then very close to the temperature-rate kinetic coefficient ($const.''' = 1.064... \text{ mK}^{-1}\text{s}^{-1}$), there is also another experimental proof for previously suggested approximation of the average value of parameter $B_{av}(x)$ [2]:

$$B_{av}(x) = const.''' = \sqrt{const.'''} = \sqrt{\text{csch}(e) + 1}. \quad (22)$$

A deeper information about the approximation of the temperature integral term $p(x)^{14}$ can be found in the following literature [17, 19–25].

2. Effective mass and derived properties of activated complex

The relation between Augis and Bennett equation (Eq. 7), $const.'''$ and $M^\#$ was already solved in the previous work as follows [2]:

$$const.''' = \frac{2.5 R}{n M^\# w_{1/2, \Theta 1}} \Rightarrow M^\# = \frac{2.5 R}{const.''' n w_{1/2, \Theta 1}} = \frac{E_a}{const.''' T_{m, \Theta 1}^2}. \quad (23)$$

Since Eq. 23 contains three constants, it is also possible to write:

$$M^\# = \frac{2.5 R}{const.''' n w_{1/2, \Theta 1}} \frac{1}{1} = 18.352 \frac{1}{n w_{1/2, \Theta 1}} = \frac{R}{const.'''} \frac{\partial \ln Q^\#}{\partial T} \Rightarrow \quad (24)$$

$$\frac{\partial \ln Q^\#}{\partial T} = \frac{const.'''}{R} M^\# = \frac{2.5}{n w_{1/2, \Theta 1}} = \frac{E_a}{R T_{m, \Theta 1}^2} = \frac{T'}{T_{m, \Theta 1}^2} = \alpha_{Q^\#} \quad [K^{-1}]$$

where $T' = E_a/R$ (please refer to Eq. 39) and $\alpha_{Q^\#}$ is the coefficient that describes how the partition function of the object changes with the change in temperature. Eq. 24 also means that the term $\partial \ln Q^\# / \partial T$ is coded directly in the shape of peak of thermoanalytical curve. Since the unit of this term corresponds to the reciprocal temperature, for example, for applied example of the process of thermal decomposition of calcite, it is possible to calculate:

¹⁴Well known approximations of $p(x)$ are provided by, e.g. Doyle [23]:

$$p(x) \cong \frac{1}{x}; \quad (a)$$

Coats and Redfern [20]:

$$p(x) \cong \left(1 - \frac{2}{x}\right) / x; \quad (b)$$

and Gorbachev [25]:

$$p(x) \cong \frac{1}{x + 2}. \quad (c)$$

$$\frac{\partial \ln Q^\ddagger}{\partial T} = \alpha_{Q^\ddagger} = 2.391 \cdot 10^{-2} K^{-1};$$

and to derive the temperature dependence of partition function on the temperature as follows:

$$Q^\ddagger(T_2) = Q^\ddagger(T_1) \exp(\alpha_{Q^\ddagger}[T_2 - T_1]).$$

Furthermore, for $n = 1$, that is, for the first (Eqs. 28–30) and pseudo-first order reactions¹⁵, the value of parameter M^\ddagger is given by the equation:

$$M^\ddagger = \frac{18.352}{w_{1/2, \Theta 1}} \Rightarrow \frac{\partial \ln Q^\ddagger}{\partial T} = \frac{2.5}{w_{1/2, \Theta 1}} [n = 1]. \quad (25)$$

For the example of thermal decomposition of calcite (Eq. 33 in Chapter 2) mentioned above, it is possible to calculate that $M^\ddagger = 0.1755 \text{ kJ} \cdot \text{mol}^{-1}$ (Table 1)¹⁶. Furthermore, Eq. 24 means that:

$$M^\ddagger \propto \frac{1}{n}. \quad (26)$$

Parameter of activated complex	E_a [kJ·mol ⁻¹]	A [10 ⁶ s ⁻¹]	n	T [K]	M^\ddagger [kg·mol ⁻¹]	V^\ddagger [m ³ ·mol ⁻¹]
	185.73	6.36	1.64	22339.4	0.1755	1.833
ρ^\ddagger [kg·m ³]	\bar{v}_x [m·s ⁻¹]	δ [m]	t_δ [s]	\bar{f}^\ddagger [kg·m ⁻² ·s ⁻¹]	\bar{p}^\ddagger [kg·m·s ⁻¹ ·mol ⁻¹]	
	9.576·10 ⁻²	1028.6	1.86·10 ⁻⁴	1.57·10 ⁻⁷	98.504	255.35

The value needs to be divided by Avogadro constant (Footnote 11 in Chapter 2) to calculate the momentum of single activated molecule, that is, $\bar{p}_{(1)}^\ddagger = 4.24 \cdot 10^{-22}$ for calcite.

Table 1. Kinetic triplet and parameters of activated complex for the process of thermal decomposition of calcite (Eq. 33 in Chapter 2).

¹⁵The concertation of one reactant in the second-order reaction of the type:



could be considered to be constant, that is, if **B** is in a great excess with respect to **A**, so its concentration remains almost unchanged during the reaction. Therefore, it can be written:

$$-\frac{d[A]}{dt} = k[A][B] = k'[A]; \quad (b)$$

where k' is the pseudo-first rate constant of the reaction.

¹⁶The substitution of data from Figure 1(a) and Table 1 to Eq. 1 enables to calculate the activation energy:

$$E_a = 1.1326 \cdot 966.55^2 \cdot 0.1755 = 185.73 \cdot 10^3 \text{ J} \cdot \text{mol}^{-1};$$

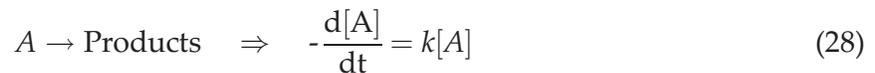
where $T_{m, \Theta 1} = 693.4 + 273,15 = 966.55 \text{ K}$ (please refer to Figure 2(a)).

The effective mass of activated state is then indirectly proportional to the reaction mechanism, the value of which is also affected by the values of T_m and $w_{1/2}$ ¹⁷ (please refer to Eq. 7). For the case of two different samples of the same species, such as two samples of calcite but of different crystallinity (1 and 2), the denominator of Eq. 25 should be very much the same value:

$$\frac{n_{(1)}}{n_{(2)}} \cong \frac{w_{1/2,(2)}}{w_{1/2,(1)}}. \quad (27)$$

This relation then introduces the law, which enables to keep the change in mass when the reactants pass into an activated state. Small observed differences are most probably caused by the combination of different isotopic compositions (please refer to Section 6 in Chapter 2), different content of admixtures in the sample and an experimental error.

The value of $M^\#$ depends on the reaction mechanism, which is technically speaking often more complicated than simply written form of chemical equation for the process. For example, Eq. 33 in Chapter 2 is formally classified as the first-order reaction of the type [26]:



which means that the rate of the process is a linear function of the concentration of reactant $[A]$, that is, there is a linear dependence of the plot $\ln [A]$ vs. time (t). The separation of variables in Eq. 28 and their integration leads to the formula:

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = - \int_0^t k dt \quad \Rightarrow \quad \ln \frac{[A]_t}{[A]_0} = -kt \quad (29)$$

so:

$$[A]_t = [A]_0 \exp(-kt). \quad (30)$$

However, the experimental value of n shows that real course of the process of thermal decomposition of calcite could be much more complicated, which is demonstrated below. It can be then concluded that the value of effective mass of activated state is affected by the mechanism of reaction. Therefore, there may not always be the direct relation to the stoichiometry of usual transcript of the reaction. It should be pointed out that scientific literature contains tremendous number of works dealing with the topic of thermal decomposition of CaCO_3 , for example [27–32], etc.

Eq. 1 can also be combined with Eq. 34 in Chapter 2 to provide the relation:

¹⁷For example, using calcite with higher sizes of crystallites leads to the increase of T_m and $w_{1/2}$ as well. Therefore, the nature of applied sample, its treatment (purification, intensive milling process, etc.) and applied conditions of analysis may also affect the mechanism of the investigated process, that is, the value of parameter $M^\#$ as well.

$$M^{\#} = \frac{-R \left(\frac{\partial \ln k}{\partial T} \right) p}{\text{const.}'' T_{m, \Theta 1}^2}. \quad (31)$$

From that it can be derived that:

$$M^{\#} = - \frac{R \ln \left(\frac{k_2}{k_1} \right)}{\text{const.}'' T_{m, \Theta 1}^2 \left(\frac{1}{T_2} - \frac{1}{T_1} \right)} \quad (32)$$

and:

$$\ln \left(\frac{k_2}{k_1} \right) = - \frac{\text{const.}'' T_{m, \Theta 1}^2 M^{\#}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right). \quad (33)$$

For the small difference between T_1 and T_2 , the approximation can also be written¹⁸:

$$\ln \left(\frac{k_2}{k_1} \right) \approx \frac{\text{const.}'' T_{m, \Theta 1}^2 M^{\#}}{R} \left(\frac{T_2 - T_1}{T_1^2} \right) \Rightarrow \quad (34)$$

$$\ln \left(\frac{k_2}{k_{(T_{m, \Theta 1})}} \right) = \frac{\text{const.}'' M^{\#}}{R} (T_2 - T_{m, \Theta 1}) \quad [T_1 = T_{m, \Theta 1}].$$

This equation can next be transformed to the formula:

$$M^{\#} \approx \frac{23}{\pi \Delta T} \ln \left(\frac{k_2}{k_1} \right). \quad (35)$$

This equation has an important implication that:

$$23 \text{ const.}'' \approx R \pi = \frac{pV^{\#}}{T'} \pi. \quad (36)$$

The combination of Eqs. (23) and (36) leads to the formula:

¹⁸The solution of the limit (refer to the right side of Eq.33):

$$\lim_{T_2 \rightarrow T_1} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = 0 = - \frac{T_2 - T_1}{T_1^2} + \frac{(T_2 - T_1)^2}{T_1^3} - \frac{(T_2 - T_1)^3}{T_1^4} + \frac{(T_2 - T_1)^4}{T_1^5} \dots;$$

can be approximated by the first term of Taylor expansion series (refer to the right side of Eq.34). The accuracy of this approximation increases as $\Delta T \rightarrow 0$, i.e. with decreasing difference between T_1 and T_2 .

$$\begin{aligned} \text{const.}'' &\approx \frac{2.5 \cdot 23}{\pi n M^\# w_{1/2}} = \frac{18.064}{n M^\# w_{1/2}} \\ &= \frac{2.875}{C_{PA}} \frac{1}{n M^\# w_{1/2}} = \frac{2.875}{C_{PT}} \frac{1}{n M^\# w_{1/2}} \end{aligned} \quad (37)$$

where C_{PA} is the Plouffe's constants and C_{PT} is the Pythagorean triple constant for the hypotenuses¹⁹. As an alternative to Eq. 33, it is also possible to write:

$$\ln \left(\frac{k_2}{k(T_{m,\Theta 1})} \right) = - \frac{\text{const.}'' T_{m,\Theta 1}^2 M^\#}{R} \left(\frac{1}{T_2} - \frac{1}{T_{m,\Theta 1}} \right). \quad (38)$$

These relations enable to describe M as the slope of plot $\ln(k_2/k_1)$ vs. $(1/T_2 - 1/T_1)$ as $\ln k_2/k(T_{m,\Theta 1})$ versus $(1/T_2 - 1/T_{m,\Theta 1})$ (**Figure 3**). The right side numerator of the last two equations is equal to E_a (Eq. 1). Eq. 33 can be applied to the isothermal as well as nonisothermal kinetic experiment, while Eq. 38 is suitable for nonisothermal experiment only.

Since the dimension of term:

$$\frac{E_a}{R} = T' = - \left(\frac{\partial \ln k}{\partial \frac{1}{T}} \right)_p, \quad \text{i.e.} \quad \left[\frac{\frac{J}{mol}}{\frac{J}{mol \cdot K}} = K \right] \quad (39)$$

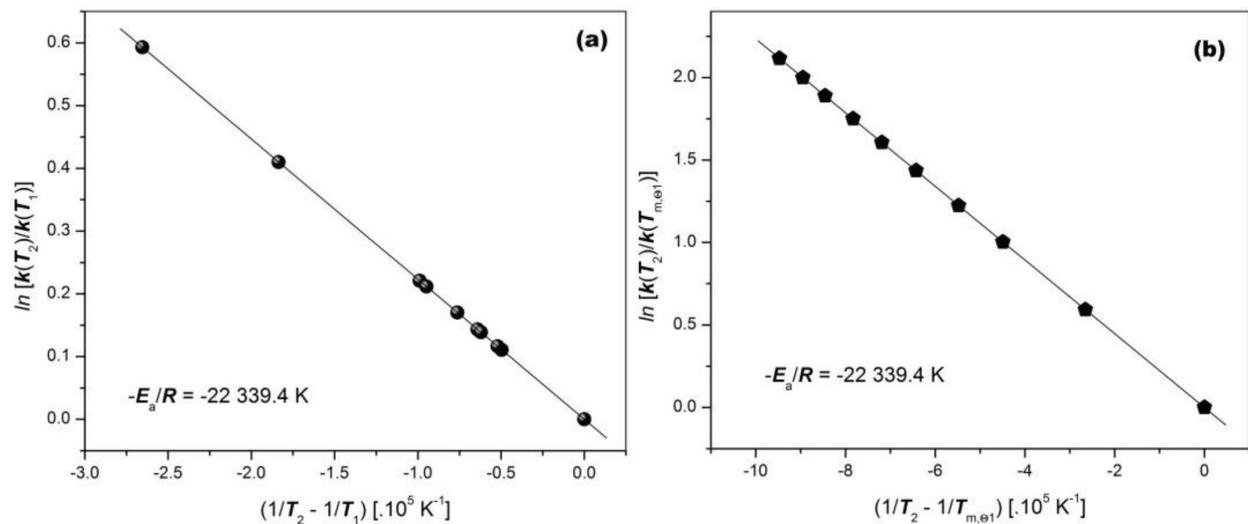


Figure 3. Graphs of $\ln(k_2/k_1)$ vs. $(T_2^{-1} - T_1^{-1})$ (a) and $\ln(k_2/k_{T_{m,\Theta 1}})$ vs. $(T_2^{-1} - T_{m,\Theta 1}^{-1})$ (b).

¹⁹ An interesting consequence of these relations is to be solved in the next article.

is equal to the temperature (temperature term of activated complex, please refer to Eqs. (80) and (81)), it is also possible to easily calculate the volume of activated state (V^\ddagger) as follows:

$$V^\ddagger = \frac{RT'}{p} = \frac{E_a}{p} = 8.205 \cdot 10^{-5} T'. \quad (40)$$

The combination with Eq. 36 in Chapter 2 then leads to the condition:

$$\frac{T'}{V^\ddagger} = \frac{T}{V_m(T)} = \frac{R}{p} \quad (41)$$

where $T'/V^\ddagger = f(T)$, so the temperature of the reaction affects the thermodynamics (stability) of activated complex, that is, the reaction rate which is given by its decomposition, (Eq. 7 in Chapter 2), but the temperature does not alter the value of activation energy. It can be further derived that:

$$\frac{V^\ddagger}{V_m(T)} = \frac{T'}{T} = \frac{E_a}{RT}. \quad (42)$$

The density of activated state could be solved to:

$$\rho^\ddagger = \frac{M^\ddagger}{V^\ddagger} = \frac{M^\ddagger p}{RT'} = \frac{p}{r^\ddagger T'} \quad (43)$$

where $r^\ddagger = R/M^\ddagger$ is the specific gas constant and $p/T' = R/V^\ddagger$ (please refer to Eq. 80 and the discussion thereof). Since:

$$M^\ddagger = \rho^\ddagger V^\ddagger = \rho^\ddagger \frac{RT'}{p} = \frac{4}{3} \pi r_{AC}^3 \rho^\ddagger. \quad (44)$$

The effective diameter of activated complex can be calculated as follows:

$$r_{AC}^\ddagger = \sqrt[3]{\frac{3 M^\ddagger}{\pi \rho^\ddagger N_A}} = \sqrt[3]{\frac{3 m_{(1)}^\ddagger}{\pi \rho^\ddagger}}. \quad (45)$$

If we consider that the velocity of activated state is equal to the term [2]:

$$\bar{v}_x = \sqrt{\frac{E_a}{M^\ddagger}}, \quad i.e. \quad \left[\sqrt{\frac{\frac{J}{mol}}{\frac{kg}{mol}}} = \frac{m}{s} \right] \quad (46)$$

and:

$$2\bar{v}_x^2 = \bar{v}^2. \quad (47)$$

Assuming the parity that for the peak of energetic barrier it is $-\bar{v}_x = \bar{v}_x$ ²⁰, it is also possible to derive that:

$$\rho^\# \bar{v}_x^2 = \frac{\rho^\# \bar{v}^2}{2} = p, \quad \text{i.e.} \quad \left[\frac{\text{kg}}{\text{m}^3} \left(\frac{\text{m}}{\text{s}} \right)^2 = \frac{\text{kg}}{\text{m s}} = \text{Pa} \right] \quad (48)$$

and then:

$$\frac{\rho^\# \bar{v}^2}{2} - p = 0. \quad (49)$$

Since the energetic density in activated volume is equal to the pressure:

$$p = \frac{E_a}{V^\#}, \quad \text{i.e.} \quad \left[\frac{\text{J}}{\frac{\text{m}^3}{\text{mol}}} = \text{Pa} \right] \quad (50)$$

more general form of Eq. 49 can be predicted:

$$\frac{\rho^\# \bar{v}^2}{2} + \rho^\# \phi - p = 0 \quad (51)$$

which was first introduced in the previous work [2]. This equation predicts the way, how the energetic density of activated state could be affected via the potential force field (ϕ).

It is possible to derive the mass velocity (mass current density or mass flux) of activated complex ($\vec{j}^\#$) in solution from the dimension of the following term:

$$\frac{E_a}{V^\# \bar{v}_x} = \left[\frac{\frac{\text{J}}{\text{mol}}}{\frac{\text{m}^3}{\text{mol}} \frac{\text{m}}{\text{s}}} = \frac{\text{kg}}{\text{m}^2 \text{s}} \right] = \vec{j}^\# = \frac{p}{\bar{v}_x} = \frac{101325}{\bar{v}_x} = \rho^\# \bar{v}_x. \quad (52)$$

Since the activation energy of the process is considered to be constant, the velocity vector of activated state does not vary with time either:

²⁰The details can be found in the previous work [2].

$$\frac{\partial \bar{v}_x}{\partial t_\delta} = 0 \quad \Rightarrow \quad \nabla \bar{v} = 0. \quad (53)$$

That means that the divergence of velocity vector is zero and the net total flux through the surface of activated complex must be equal to zero.

Since the dimension of term:

$$\delta = \frac{\bar{v}_x}{A} = \frac{\sqrt{\frac{E_a}{M^\ddagger}}}{A} = 24 \bar{v}_x w_{1/2, \Theta 1} \exp\left(-\frac{E_a}{RT_{m, \Theta 1}}\right) [m] \quad (54)$$

has a physical meaning of length, it is possible to calculate the length of energetic barrier (δ) from this relationship. From the combination of Eq. 54 with the Arrhenius equation, it can also be derived that $w_{1/2, \Theta 1} k(T_{m, \Theta 1}) = 1/24$. Therefore, the rate constant for the peak temperature $T_{m, \Theta 1}$ can be directly calculated ($k(T_{m, \Theta 1}) = 1/(24 w_{1/2, \Theta 1})$) using full width at half maximum of peak measured with the heating rate $\Theta = 1 \text{ K} \cdot \text{min}^{-1}$.

The mean lifetime of activated complex (t_δ), that is, the time, which is required to overcome the energetic barrier is then equal to:

$$t_\delta = \frac{\delta}{\bar{v}_x} = A^{-1} = \frac{\exp\left(-\frac{E_a}{RT}\right)}{k(T)} = 1.443 t_{1/2} \quad \Rightarrow \quad A = \frac{1}{t_\delta} = \frac{1}{\delta} \sqrt{\frac{E_a}{M^\ddagger}} \quad (55)$$

where $t_{1/2} = \ln 2/A = t_\delta \ln 2$ is the half-life of activated complex. That means that the concentration of activated complex can be written in terms of the exponential decay equation (please refer also to Eq. 7 in Chapter 2):

$$[C^\ddagger]_t = [C^\ddagger]_0 \exp(-At);$$

where term $At = t/t_\delta$ ($At_\delta = 1$) and $[C^\ddagger]_t$ and $[C^\ddagger]_0$ are the concentrations of activated complexes at time t and $t = 0$, that is, the initial quantity. This formula then enables to write:

$$\begin{aligned} k(T) &= -\frac{1}{t} \ln \frac{[C^\ddagger]_t}{[C^\ddagger]_0} \exp\left(-\frac{E_a}{RT}\right) \Rightarrow k(T) = \frac{\ln e}{t_\delta} \exp\left(-\frac{E_a}{RT}\right) \Rightarrow \ln k(T) \\ &= \ln \frac{1}{t_\delta} - \frac{E_a}{RT} \left[t = t_\delta \Rightarrow [C^\ddagger]_t = \frac{[C^\ddagger]_0}{e} \right]; \end{aligned}$$

(please refer also to Eq. 20 in Chapter 1 and to discussion of Eq. 27 in Chapter 2). The effective rate of activated complex²¹ can be then formulated as follows:

²¹It is also interesting to apply the Albert Einstein's (1879–1955) special theory of relativity (STR), where it is possible to calculate the invariant mass of activated state as follows:

$$m_{(1)}^{\#,0} = m_{(1)}^{\#} \sqrt{1 - \frac{\bar{v}^2}{c^2}}; \quad (a)$$

which is, e.g. for calcite $2.915 \cdot 10^{-25}$ kg. Since activated on the peak of energetic barrier, it has the kinetic energy only (please refer to the discussion of Eqs. 79 and 82 in Section 4), it can further be written:

$$\frac{E_a}{N_A} = E_{(1)} = E_{k(1)} = m_{(1)}^{\#} c^2 - m_{(1)}^{\#,0} c^2 = \left(\frac{1}{\sqrt{1 - \frac{\bar{v}^2}{c^2}}} - 1 \right) m_{(1)}^{\#,0} c^2 = (\gamma - 1) m_{(1)}^{\#,0} c^2; \quad (b)$$

where the subscript (1) denotes the value pertinent to one activated molecule, i.e. the molar value divided by the Avogadro constant (Footnote 11 in Chapter 2), c is the speed of light in vacuum and the term:

$$\left(\frac{1}{\sqrt{1 - \frac{\bar{v}^2}{c^2}}} \right) = \frac{1}{\sqrt{1 - \beta_v^2}} = \gamma; \text{ where } \beta_v = \frac{\bar{v}}{c}; \quad (c)$$

is known as the Lorentz factor (Lorentz term), which was named after Dutch physicist Hendrik Antoon Lorentz (1853–1928, awarded by Nobel prize for Physics in 1902). Since the dimensionless rate ratio of activated complex to the speed of light β_v is very low the value of $\gamma \rightarrow 1$, e.g. 1.00000000001177 for calcite. It can be then verified that:

$$\begin{aligned} E_a &= E_{(1)} N_A = E_{k(1)} N_A = (\gamma - 1) m_{(1)}^{\#,0} c^2 = \\ &= (1.00000000001177 - 1) \cdot 2.915 \cdot 10^{-25} \cdot 299792458^2 \cdot 6.022 \cdot 10^{23} = 185.73 \cdot 10^3 \text{ J} \cdot \text{mol}^{-1}. \end{aligned} \quad (d)$$

Please compare this value to data in **Table 1**. Using special theory of relativity, the energy of activated state can be expressed as follows:

$$E \approx m_{(1)}^{\#,0} c^2 + E_{(1)} = m_{(1)}^{\#,0} c^2 + \frac{1}{2} m_{(1)}^{\#} \bar{v}^2; \quad (e)$$

i.e. as the sum of Einstein's mass-energy equivalence formula ($E = mc^2$) and kinetic (activation) energy. That enables to formulate the energy ratio:

$$o = \frac{E_{(1)}}{m_{(1)}^{\#,0} c^2}. \quad (f)$$

The value of this ratio is $1.177 \cdot 10^{-11}$ and $1.2 \cdot 10^{-11}$ for in this book investigated samples of calcite and aragonite, respectively. The relation between o and β_v is given by the formula:

$$1 - \beta_v^2 = \frac{1}{(1 + o)^2}. \quad (g)$$

For the effective mass (h), the velocity (ch) and the momentum (i) of activated complex, the relations can be then written:

$$m_{(1)}^{\#} = m_{(1)}^{\#,0} (1 + o) = \frac{m_{(1)}^{\#,0}}{\sqrt{1 - \beta_v^2}}; \quad (h)$$

$$\bar{v} = c \frac{\sqrt{(1 + o)^2 - 1}}{1 + o}; \quad (i)$$

and:

$$\bar{p}_{(1)}^{\#} = m_{(1)}^{\#,0} c \sqrt{(1 + o)^2 - 1}. \quad (j)$$

$$\bar{v}_x = \frac{\delta}{t_\delta} = \sqrt{\frac{E_a}{M^\#}} \Rightarrow E_a = M^\# \bar{v}_x^2 = \frac{1}{2} M^\# \bar{v}^2 = E_k \quad (56)$$

for the peak of energetic barrier.

The effective rate of activated complex (Eqs. 46, 47 and 56) can also be formulated using the relation for the speed of sound in ideal gas as follows:

$$\bar{v}_x = \sqrt{\frac{p}{\rho^\#}} \quad (57)$$

and:

$$\bar{v} = \sqrt{\gamma \frac{p}{\rho^\#}} = \sqrt{2 \frac{p}{\rho^\#}} \quad (58)$$

where γ is the value of adiabatic index, that is, the isentropic expansion factor. The value of this index is given by the ratio:

$$\lambda = \frac{c_{pm}}{c_{vm}} = \frac{2R}{R} = 2 = \frac{\Delta H^\#}{\Delta U^\#} \quad (59)$$

where $\Delta U^\#$ is the internal energy of activation. From Eq. 58, it can be further derived that:

$$\bar{v} = \sqrt{2 \frac{p}{\rho^\#}} = \sqrt{2 \frac{RT'}{M^\#}} = \sqrt{2 \frac{E_a}{M^\#}} = \sqrt{2 \frac{kT'}{m_{(1)}^\#}}. \quad (60)$$

Since:

$$\bar{v} = \sqrt{\frac{K_B}{\rho^\#}} \quad (61)$$

the bulk modulus of activated complex can also be calculated as follows:

$$K_B = \rho^\# \bar{v}^2 = 2p. \quad (62)$$

The nature of velocities \bar{v}_x and \bar{v} can also be easily solved from the statistic probability function known as the Maxwell-Boltzmann distribution:

$$F(\bar{v}^2) = \sqrt{\frac{2}{\pi}} n_P \left(\frac{m}{k_B T} \right)^{3/2} \exp \left(\frac{-m \bar{v}_P^2}{2k_B T} \right) \bar{v}_P^2 \quad (63)$$

where n_P is the number of particles with the velocity \bar{v}_P . With regard to the translation energy (Eq. 56) and two degrees of freedom [2] of activated state, it can then be written:

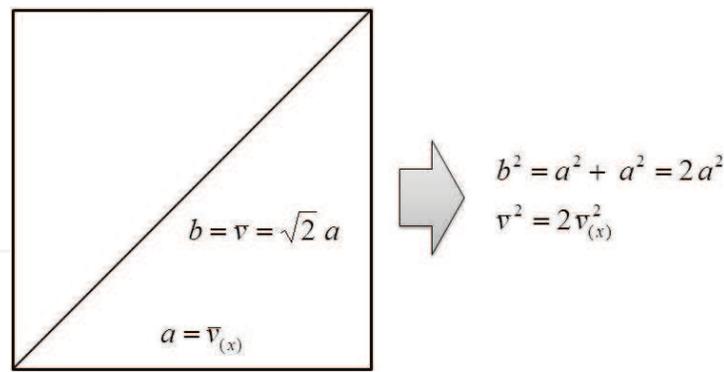


Figure 4. The relation between \bar{v}_x and \bar{v} . Please refer to Eqs.47 and 68.

$$F(\bar{v}^2) = \sqrt{\frac{2}{\pi}} \left(\frac{M^\#}{RT'} \right) \exp \left(-\frac{M^\# \bar{v}^2}{2RT'} \right) \bar{v}^2. \quad (64)$$

This relation can be further transformed to the following formula:

$$F(\bar{v}^2) = \frac{\sqrt{\frac{2}{\pi}}}{\bar{v}_x^2} \frac{\bar{v}^2}{e} = \frac{\sqrt{\frac{2}{\pi}}}{a^2} \frac{b^2}{e} \quad (65)$$

where the scale parameter of Maxwell–Boltzmann distribution (a) is:

$$a = \bar{v}_x = \sqrt{\frac{RT'}{M^\#}} \Rightarrow \frac{1}{a^2} = \frac{M^\#}{RT'} = \frac{1}{\bar{v}_x^2} = \frac{1}{const. T_{m, \Theta 1}^2} \quad (66)$$

and the mode of Maxwell-Boltzmann distribution (b) is:

$$b = \bar{v} = a\sqrt{2} \quad (67)$$

that is, the diagonal of the square with the side length equal to $a = \bar{v}_x$ (Figure 4).

These equations Eqs. 64–66 also define the role of *const.*" (Eq. 1) in the Maxwell–Boltzmann distribution. Furthermore, Eq. 65 can be solved as follows:

$$0.58705\dots = \frac{2}{e} \sqrt{\frac{2}{\pi}} = \sqrt{\frac{2}{\pi}} \frac{\bar{v}^2}{e \bar{v}_x^2} \Rightarrow \frac{\bar{v}^2}{\bar{v}_x^2} = 2. \quad (68)$$

Eq. 68 then also provides an important proof for the validity of Eq. 47. From this point of view, the velocities \bar{v}_x and \bar{v} are the scale factor and the mode, that is, the most probable speed, in Maxwell-Boltzmann distribution, respectively. Furthermore, it can also be written that:

$$M^\# = \frac{-2E_a \ln \left(\frac{1}{e} \right)}{\bar{v}^2} = \frac{2E_a \ln (e)}{b^2} = \frac{E_a}{\bar{v}_x^2}. \quad (69)$$

Eq. 67 means that all activated complexes have constant values of the ratio:

$$\frac{\bar{v}}{\bar{v}_x} = 1.4142\dots = \sqrt{2} = M_a \quad (70)$$

where M_a is the Mach number, which is defined as the dimensionless ratio of velocity of object and of speed of sound in given medium, that is in this particular case it is the ratio of \bar{v} and \bar{v}_x (Eqs. 47 and 68), respectively. With regard to the most probable rate of activated complex (mode of the Maxwell-Boltzmann distribution, Eq. 64), the translation of activated molecule along the reaction coordinate is always supersonic.

The combination of Eq. 70 with Eqs. (1) and (56) then leads to the formula:

$$E_a = \frac{M_a^2}{2} M^\# \bar{v}_x^2 = M^\# \bar{v}_x^2. \quad (71)$$

Furthermore, the combination of Eqs. (56) and (71) leads to the relation between both \bar{v} and \bar{v}_x , that is, to Eq. 47.

The values of \bar{v} and \bar{v}_x are also related to the velocity of De Broglie's "phase wave" (phase velocity $\bar{v}_p = E_a/\bar{p}^\# = \lambda^\#/T^\# = \omega^\#/\bar{k} \Rightarrow E_a = (\omega^\#\bar{p}^\#)/\bar{k}$), which should occur in the phase with intrinsic particle periodic phenomenon [33]. The relation between these velocities can then be expressed by the formula:

$$\bar{v} = \sqrt{2} \bar{v}_x = 2 \bar{v}_p = 2 \frac{E_a}{\bar{p}^\#} = 2 \lambda^\# \nu^\# = \frac{\bar{p}_{(1)}^\# c^2}{\sqrt{c^2 \bar{p}_{(1)}^{\#2} + m_{(1)}^{\#,0^2} c^4}} \quad (72)$$

where $m_{(1)}^{\#,0}$ is the invariant mass of activated complex (please refer to Eq. (a) in Footnote 21). Therefore, the ratio of $\bar{v} : \bar{v}_x$ (Eq. 70) has exactly the same value as the ratio of $\bar{v}_x : \bar{v}_p$:

$$\frac{\bar{v}}{\bar{v}_x} = \frac{\bar{v}_x}{\bar{v}_p} = \sqrt{2} = 1.4142\dots \quad (73)$$

so:

$$\bar{v}_x = \sqrt{2} \bar{v}_p. \quad (74)$$

It is then obvious that \bar{v}_x is the diagonal of the square with the side length equal to \bar{v}_p . Since the ratio:

$$\bar{v}^2 : \bar{v}_x^2 : \bar{v}_p^2 = 1 : 2 : 4 \quad (75)$$

the squares of these velocities (\bar{v}^2 , \bar{v}_x^2 and \bar{v}_p^2) then form a geometric sequence (**Figure 5**) with common ratio = 2 (Eq. 68).

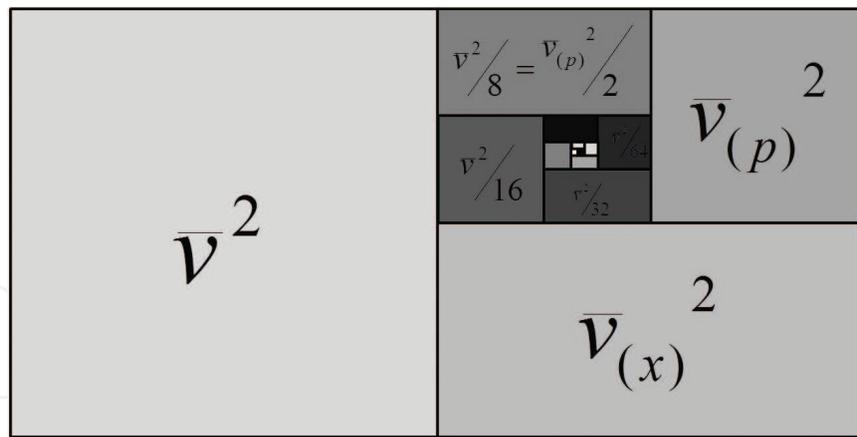


Figure 5. The diagram showing the geometric series of \bar{v}^2 , \bar{v}_x^2 and \bar{v}_p^2 .

The values of \bar{v}^2 , \bar{v}_x^2 and \bar{v}_p^2 for the example of thermal decomposition of calcite and aragonite applied in this book are:

529045.43: 1058090.86: 2116181.72;

and

539291.80: 1078583.61: 2157167.22;

respectively. That also enables to express the value of \bar{v}_x^2 as the geometric ratio of \bar{v}^2 and \bar{v}_p^2 :

$$\bar{v}_x^2 = \sqrt{\bar{v}^2 \bar{v}_p^2}. \quad (76)$$

Therefore, the quantum numbers of activated complex, that is, the activation energy and the momentum of activated complex, enable to express the following three velocities, that is:

1. The group velocity of a supersonic activation wave, which is equal to the most probable velocity (mode) resulting from the Maxwell-Boltzmann distribution (\bar{v}).
2. Sonic dissipation (shock) wave, which corresponds to the velocity of sound. This velocity (scale parameter of Maxwell-Boltzmann distribution) is termed in this work as the effective speed of activated complex (\bar{v}_x).
3. Phase velocity, that is the subsonic De Broglie "phase wave" (\bar{v}_p), which is equal to the speed at which the phase of the wave propagates in given medium.

That behavior makes it possible to suggest the theory that the formation of activated complex (reversible process, please refer to Chapter 2) also generates the irreversible dissipative wave (shock wave). This discontinuity in the pressure, temperature and density preserves the energy, but increases the system entropy. That means that the formation of activated state (activated

Parameter of Activated complex	E_a [kJ·mol ⁻¹]	A [10 ⁷ s ⁻¹]	n	T^* [K]	M^\ddagger [kg·mol ⁻¹]	V^\ddagger [m ³ ·mol ⁻¹]
	199.38	3.86	1.86	23981.8	0.1849	1.968
	ρ^\ddagger [kg·m ³]	\bar{v}_x [m·s ⁻¹]	δ [m]	t_δ [s]	\bar{j}^\ddagger [kg·m ⁻² ·s ⁻¹]	\bar{p}^\ddagger [kg·m·s ⁻¹ ·mol ⁻¹]
	9.394·10 ⁻²	1038.5	3.39·10 ⁻⁴	2.59·10 ⁻⁸	97.564	271.51

The value needs to be divided by Avogadro constant (Footnote 11 in Chapter 2) to calculate the momentum of single activated molecule, that is, $\bar{p}_{(1)}^\ddagger = 4.53 \cdot 10^{-22} \text{ kg} \cdot \text{m} \cdot \text{s}^{-1}$ for aragonite.

Table 2. Kinetic triplet and parameters of activated complex for the process of thermal decomposition of aragonite (Eq. 33 in chapter 2).

molecule and shock wave) causes increasing entropy of the system, even in the case, that activated complex decomposes back to the reactants.

Also, there is really interesting fact that \bar{v} which relates to the process of thermal decomposition of calcite (**Table 1**) and aragonite (**Table 2**), is of the magnitude, which corresponds to the rate of sound or ultrasound in liquids (please refer also to the discussion of Eq. 56), for example, 1497 m·s⁻¹ in distilled water at 25°C. Since only the longitudinal wave²² can be propagated in liquids and gases (fluids in general), the activated complex can oscillate (transfer energy) along the direction of the reaction coordinate only. It can be then derived:

$$\bar{v}_x^2 = \frac{p}{\rho^\ddagger} = \frac{E_a}{M^\ddagger} = \frac{\bar{v}^2}{2} = \text{const.}'' T_{m,\Theta 1}^2 \quad (77)$$

and then:

$$\begin{aligned} \bar{v}^2 &= 2 \text{const.}'' T_{m,\Theta 1}^2 \Rightarrow \\ \bar{v} &= \sqrt{2 \text{const.}'' T_{m,\Theta 1}^2} = 1.505 \dots T_{m,\Theta 1} \approx \sqrt{\frac{5e}{6}} T_{m,\Theta 1} \end{aligned} \quad (78)$$

Then there is direct proportionality between \bar{v} and $T_{m,\Theta 1}$, where the value of proportionality constant is $\sqrt{2 \text{const.}''}$. From this, it can be calculated that the most probable rate of activated complex is equal to the speed of sound in air (346.3 m·s⁻¹, dry air at 25°C) and water (1497 m·s⁻¹) for $T_{m,\Theta 1}$ equal to 230.1 and 994.7 K, respectively.

Since further increasing of temperature increases the rate of activated complex as well, so it becomes comparable with the speed of sound in the solids, it can then also be deduced that increasing the temperature of the process ($T_{m,\Theta 1}$) increases the probability of oscillation in the direction perpendicular to the reaction coordinate, that is, the activated state can get additional

²²On the contrary, the longitudinal as well as transversal waves (oscillate perpendicular to the direction of energy transfer) can propagate in the solids.

degrees of freedom. The energy which is stored in those additional degrees of freedom then increases the energetic density of activated complex, which is on the contrary reduced by the value of V^\ddagger which increases with temperature (Eq. 81).

Therefore, there is a possibility to formally divide the reactions according to the behavior of activated state described above, as follows:

1. Reaction with most probable (group) velocity of activated state in fluid region, that is the value of \bar{v} is comparable to the speed of sound in gases and liquids. It can be potentially divided to the subregion of gases and liquids.
2. Reaction with most probable velocity of activated state in solid region, that is the value of \bar{v} is comparable to the speed of sound in solids.

3. Introducing the quantum numbers of activated complex

Since the effective mass and the velocity of activated state are known, it is also possible to calculate the momentum per mol of activated states²³ as follows²⁴:

$$\bar{p}^\ddagger = M^\ddagger \bar{v} = \bar{p}_{(1)}^\ddagger N_A = N_A \hbar \bar{k} = \frac{N_A h}{\lambda^\ddagger} \quad (79)$$

and to formulate the activation energy using the constitutive equation of the state of activated complex:

$$f(p, V^\ddagger, T') = 0 \quad (80)$$

that is:

$$RT' = pV^\ddagger \Rightarrow \frac{V^\ddagger}{V} = \frac{T'}{T} = \frac{E_a}{RT} = \frac{E_a}{pV} \quad (81)$$

as follows:

$$E_a = \frac{\bar{p}^{\ddagger 2}}{2 M^\ddagger} = \frac{N_A^2 \hbar^2 \bar{k}^2}{2 M^\ddagger} = N_A h v_{AC}^\ddagger = RT' = pV^\ddagger \quad (82)$$

²³The calculation of momentum per particle then requires to divide Eq. 79 by N_A (Footnote 11 in Chapter 2).

²⁴Eq. 79 then corresponds to the de Broglie matter waves (Louis Victor Pierre Raymond de Broglie, 1892–1987, Nobel Prize in Physics in 1929).

where \hbar is reduced Planck (Dirac²⁵) constant²⁶, \bar{k} is the wave vector, $\lambda^\# = h/p^\#_{(1)}$ is the de Broglie wavelength²⁷ and $\nu^\#_{AC} = (k_B T)/h$ (please refer to Eq. 115 and Eq. 27 in Chapter 2) is the universal frequency of activated complex. Eq. 81 also means that the pressure can affect the temperature and the rate constant of process, but the value of activation energy should be independent of the pressure. The combination of Eq. 29 in Chapter 2 with Eq. 81 then leads to the formula²⁸:

$$E_a = p \int_{V_m(T)}^{V^\#} dV + RT = p (V^\# - V_m(T)) + RT = R (T' - T) + RT \quad (83)$$

that is the effect of reaction temperature on enthalpy of activation (corresponds to the work of isobaric process) lays in the reduction of $\Delta H^\#$ for reversible isobaric work $-p \cdot [V_m(T_2) - V_m(T_1)] = -R\Delta T$ (**Figure 6**), and then:

$$\frac{E_a}{RT} = \frac{p}{RT} \int_{V_m(T)}^{V^\#} dV + 1 = \frac{\Delta V}{V_m(T)} + 1 = \frac{T'}{T} \quad (84)$$

where $\Delta V = V^\# - V_m(T)$. Eq. 84 could be further treated as follows:

²⁵Named after English physicist Paul Dirac (1902–1984). Dirac was awarded the Nobel Prize in Physics in 1933.

²⁶Reduced Planck constant is the ratio:

$$\hbar = \frac{h}{2\pi} = 1.054571800 \cdot 10^{-34} \text{ J} \cdot \text{s} \cdot \text{rad}^{-1}; \quad (a)$$

or the product:

$$\hbar = E_p t_p = \frac{E_p L_p}{c} \Rightarrow h = 2\pi E_p t_p = \frac{2\pi E_p L_p}{c}; \quad (b)$$

where E_p is the Planck energy (the derived Planck unit):

$$E_p = \sqrt{\frac{\hbar c^5}{G}} = \frac{\hbar}{t_p} \approx 1.956 \cdot 10^9 \text{ J}; \quad (c)$$

t_p is the Planck time (the basic Planck unit):

$$t_p = \sqrt{\frac{\hbar G}{c^5}} = \frac{\hbar}{E_p} \approx 5.391 \cdot 10^{-44} \text{ s}; \quad (d)$$

$c = 299,792,458 \text{ m} \cdot \text{s}^{-1}$ is the speed of light in a vacuum and G is the Gravitational (Universal or Newton's) constant ($6.67408 \cdot 10^{-11} \text{ m}^3 \cdot \text{kg}^{-1} \cdot \text{s}^{-2}$). The other four basic Planck units are the Planck length:

$$L_p = \sqrt{\frac{\hbar G}{c^3}} \approx 1.616 \cdot 10^{-35} \text{ m}; \quad (e)$$

The Planck mass, the Planck electric charge and the Planck temperature.

²⁷Please refer also to Eq. 11 in Chapter 2.

²⁸For example, the molar volume of ideal gas at the temperature of 966.55 K (according to **Figure 1** and **Figure 2(b)**) this temperature corresponds to thermal decomposition of calcite at the heating rate of $1 \text{ K} \cdot \text{min}^{-1}$) is $V_m = RT/p = 7.931 \cdot 10^{-2} \text{ m}^3 \cdot \text{mol}^{-1}$, so Eq. 83 provides the value $E_a = -101,325 \cdot (7.931 \cdot 10^{-2} - 1.833) + 8.314 \cdot 966.55 = 185.73 \cdot 10^3 \text{ kJ} \cdot \text{mol}^{-1}$. Please compare to the value in **Table 1**.

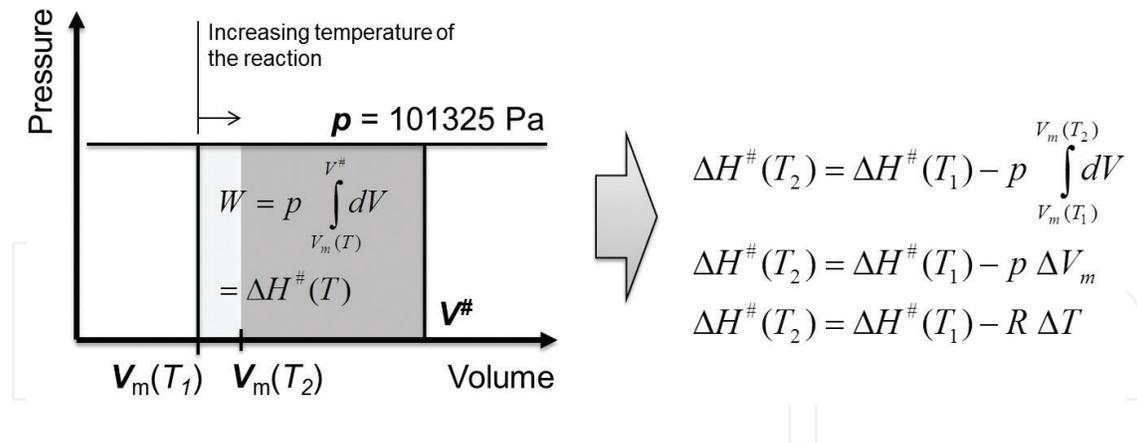


Figure 6. The influence of temperature on the enthalpy of activation. This topic as well as the temperature dependence of ΔS^\ddagger is also described in previous work [2].

$$\frac{E_a}{RT} - 1 = \frac{1}{V_m(T)} \int_{V_m(T)}^{V^\ddagger} dV = \frac{V^\ddagger}{V_m(T)} - 1 \quad (85)$$

so:

$$\frac{E_a}{RT} = \frac{V^\ddagger}{V_m(T)} \Rightarrow E_a V_m(T) = RT V^\ddagger. \quad (86)$$

From Eq. 86 it can then be easily verified that $E_a = pV^\ddagger = RT$ (Eq. 82). Therefore, if $E_a > 0$ (activated processes) the value of $V^\ddagger > V_m(T) \Rightarrow \Delta V > 0$ (the activated complex does a positive work), so $E_a > RT$.

Before we continue with quantum numbers of activated complex, it is interesting to mention that Eqs. (79) and (82) allow to solve the relation of these numbers (the activation energy and the momentum) to the Gravitational constant (G), for example, as follows:

$$\bar{p}^\ddagger = N_A \frac{L_p^2 c^3}{G} \bar{k} \quad (87)$$

and:

$$E_a = \frac{N_A^2 L_p^4 c^6 \bar{k}^2}{2 M^\ddagger G^2} = \frac{1}{2} M^\ddagger \bar{v}^2. \quad (88)$$

As results from footnote 29, there are other equations analogical to the Planck energy²⁶ (E_p , Eq. (c)):

$$\bar{p}^\ddagger = N_A \frac{E_p^2 G}{c^5} \bar{k} \quad (89)$$

and:

$$E_a = \frac{N_A^2 E_p^4 G^2 \bar{k}^2}{2 M^\# c^{10}} \quad (90)$$

or to the Planck time²⁶ (t_p , Eq. (e)):

$$\bar{p}^\# = N_A \frac{t_p^2 c^5}{G} \bar{k} = \frac{N_A Y \bar{k}}{G} = N_A \hbar \bar{k} \quad (91)$$

and then the relation:

$$E_a = \frac{N_A^2 t_p^4 c^{10} \bar{k}^2}{2 M^\# G^2} = \frac{N_A^2 Y^2 \bar{k}^2}{2 M^\# G^2} = \frac{N_A^2 \hbar^2 \bar{k}^2}{2 M^\#} \quad (92)$$

can be easily formulated. It can also be clearly seen that:

$$\begin{aligned} L_p^2 c^3 &= t_p^2 c^5 = \frac{E_p^2 G^2}{c^5} = \frac{\bar{p}^\# G}{N_A \bar{k}} = \frac{2 E_a M^\# c^5}{N_A^2 \bar{k}^2 E_p^2} \\ &= Y \approx 7.0383 \cdot 10^{-45} = \frac{1.866 \cdot 10^{-26} c^2 \bar{p}_{(1)}^\#}{8 \pi \bar{k}} \end{aligned} \quad (93)$$

where $1.866 \cdot 10^{-26} m \cdot kg^{-1} = (8 \pi G)/c^2$ is the Einstein's constant (the coupling constant in the Einstein field equation), which is directly proportional to the gravitational constant, constant term Y and activation energy as well (Eq. 93). The dimension of this constant term Y can be derived, for example, from Eq. 93 as follows:

$$\frac{2 E_a M^\# c^5}{N_A^2 \bar{k}^2 E_p^2} \Rightarrow \left[\frac{\frac{J}{mol} \frac{kg}{mol} \left(\frac{m}{s}\right)^5}{\left(\frac{1}{mol}\right)^2 \left(\frac{1}{m}\right)^2 J^2} = \frac{kg m^7}{J s^5} = \frac{m^5}{s^3} \right]. \quad (94)$$

All abovementioned equations for the calculation of momentum and activation energy (Eqs. 87–92) contain this term (Y) in the numerator. It can then be written that:

$$G = \frac{N_A Y \bar{k}}{\bar{p}^\#} = \frac{Y \bar{k}^\#}{\bar{p}_{(1)}} \quad (95)$$

Using, for example Eq. 91, the relation can further be derived:

$$\frac{\bar{p}^\#}{\bar{k}} = \frac{N_A Y}{G} = N_A \hbar \quad (96)$$

and Eq. 92:

$$\frac{2M^\#E_a}{\bar{k}^2} = \left(\frac{N_A Y}{G}\right)^2 = N_A^2 \hbar^2. \quad (97)$$

It can also be verified that:

$$\bar{p}^\# = \sqrt{2M^\#E_a} = M^\#\bar{v} \quad (98)$$

and:

$$\bar{v}^2 = \frac{2E_a}{M^\#} \Rightarrow E_a = \frac{1}{2}M^\#\bar{v}^2. \quad (99)$$

The motion of activated complex can then be fully characterized by two numbers, that is the activation energy and the momentum, which are directly proportional to physical action $Y/G = \hbar$. Therefore, these two numbers can be considered as the quantum numbers of activated complex.

4. Formulation of wave function, reduced mass and relative velocity of activated complex

Using the momentum, the mass activation energy, etc., for one molecule of activated complex^{20,23}, the Avogadro constant is left out from these relations. Furthermore, the quantum numbers of activated state and its mass can then be defined in terms of universal physical constants, for example, the Gravitational constant, reduced Planck constant and the speed of light in the vacuum.

The important consequences of relations 79 and 82 are the following:

1. The activated complex at the peak of energetic barrier, which represent the equilibrium, but not a stable state, has the kinetic energy (momentum) only.
2. The complete characterization of the motion of activated complex alongside the reaction coordinate requires the knowledge of two its quantum numbers:
 - a. Activation (kinetic) energy, it is obvious that activated processes have $E_a > 0$;
 - b. Momentum of activated complex.
3. There is not any quantization either for the energy or for the momentum of activated state.
4. The shift from the equilibrium position (the peak of energetic barrier and the bottom of potential well at the same time) decreases the kinetic energy and increases the potential energy of activated complex.

The expression of $M^\#$ from Eq. 82 leads to the formula:

$$M^\# = \frac{1}{E_a} \frac{(\hbar \bar{k} N_A)^2}{2} = 2.017 \cdot 10^{-21} \frac{\bar{k}^2}{E_a}. \quad (100)$$

The substitution for E_a (Eq. 1) in this formula then enables to write:

$$\text{const.}^\# = \frac{1}{2} \left(\frac{\hbar \bar{k} N_A}{T_{m, \Theta} M^\#} \right)^2 \quad (101)$$

and:

$$p = \frac{(N_A \hbar \bar{k})^2}{2M^\# V^\#} = \frac{\rho^\# \bar{v}^2}{2} \quad (102)$$

where:

$$\bar{v} = \frac{2E_a}{\bar{p}^\#} = \frac{2E_a}{\bar{p}_{(1)} N_A}. \quad (103)$$

From the discussion above, it can then be concluded, that the definition of change in mass when the reactants pass into the activated state, enables to calculate many important parameters of activated complex. It is then feasible to use the Schrödinger equation²⁹ for the description of its behavior, but the solution is in the same form as for classical physics:

$$E_a = \frac{(N_A \hbar \bar{k})^2}{2M^\#} = N_A \hbar \omega^\# \quad (104)$$

where:

$$\omega^\# = \frac{E_a}{N_A \hbar} = \frac{N_A \hbar \bar{k}^2}{2 M^\#} \quad (105)$$

is an angular frequency which is related to the “ordinary” universal frequency of activated complex $\nu_{AC}^\#$ ($\nu_{AC}^\#/\nu^\# = (E_a/RT) = \ln A/k + 1/e$, please refer to Eq. 27 in Chapter 2 \Rightarrow the reaction rate constant ratio $k_{Arhenius}/k_{Eyring} = 1/e \approx 1/2.71828 = 0.36788$) via the relation:

²⁹Erwin Rudolf Josef Alexander Schrödinger (1887–1961). The Schrödinger’s equation describes the behavior (evolution with time) of a physical system in which the quantum effects, such as the particle-wave duality take place:

$$i\hbar \frac{\partial \psi(\vec{r}, t)}{\partial t} = \hat{H} \psi(\vec{r}, t); \quad (a)$$

where i is the imaginary unit, $\hbar = h/2\pi$ is reduced Planck constant, ψ is the wave function (ψ), \vec{r} is the position vector, t is the time. The Hamiltonian (evolutional) operator:

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar}{2m} \nabla^2 + V(\vec{r}, t); \quad (b)$$

where \hat{T} is the kinetic and \hat{V} is the potential energy operator, characterizes the total energy of wave function. This operator was named after Irish physicist, astronomer and mathematician William Rowan Hamilton (1805–1865) who was awarded the Royal Medal (The King’s (Queen’s) Medal) in 1835.

$$\omega^\# = 2\pi\nu_{AC}^\# = 2\pi \frac{E_a}{hN_A}. \quad (106)$$

It is obvious that the activated complex behaves as the pseudoparticle (instanton) that corresponds to one dimensional, that is the reaction coordinate (r), plane wave with the equation:

$$\psi(r, t) = e^{(E_{(1)}t - \bar{p}_{(1)}^\# r) / (i\hbar)} \quad (107)$$

where r (please refer to the discussion of Eq. 113) is the shift of activated complex from equilibrium position (the peak of energetic barrier) and the value of $E_{(1)} = E_a/N_A$ and the Hamiltonian³¹ is equal to the kinetic energy operator:

$$\hat{H} = \hat{T} = \frac{\hat{p}^2}{2m_{(1)}^\#} = \frac{(-i\hbar\nabla)^2}{2m_{(1)}^\#} = \frac{(-i\hbar)^2}{2m_{(1)}^\#} \Delta = -\frac{\hbar^2}{2m_{(1)}^\#} \frac{\partial^2}{\partial r^2} \quad (108)$$

where ∇ is the nabla (del) operator³⁰ and $\Delta = \nabla^2 = \nabla \cdot \nabla$ is the Laplace operator³¹ (Laplacian). The pertinent kinetic energy of activated complex is then given by the formula:

$$E_{(1)} = \frac{\bar{p}_{(1)}^{\#2}}{2m_{(1)}^\#} = \frac{\bar{p}^{\#2}}{2M^\#N_A} = k_B T_{m, \Theta 1}^2 \frac{\partial \ln Q^\#}{\partial T} = \frac{E_a}{N_A} \quad (109)$$

where $m_{(1)}^\# = M^\# / N_A$ and the operator:

$$\hat{p} = -i\hbar\nabla = -i\hbar \frac{\partial}{\partial r} \quad (110)$$

has the momentum:

$$\bar{p}_{(1)}^\# = \pm \hbar \bar{k} = \pm \sqrt{2m_{(1)}^\# E_{(1)}} = \pm \frac{\bar{p}^\#}{N_A}. \quad (111)$$

The commutation of operators \hat{T} and \hat{p} then means that:

³⁰The vector differential operator "nabla" in three dimensional coordinate system with the basis vectors \bar{i}, \bar{j} and \bar{k} and is written as:

$$\nabla = \bar{i} \frac{\partial}{\partial x} + \bar{j} \frac{\partial}{\partial y} + \bar{k} \frac{\partial}{\partial z}.$$

³¹The differential operator given by the divergence of gradient of a function in Euclidian space:

$$\Delta = \nabla \cdot \nabla = \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2};$$

which was named after the mathematician Euclid of Alexandria. The formulation of del or Laplacian depends on the coordinate system applied, that is, Cartesian, cylindrical and spherical coordinate.

$$[\hat{T}, \hat{p}] = 0. \quad (112)$$

The solution of motion of activated complex (state) mentioned above enables to consider it and treat it as an instanton, that is a pseudoparticle. The pertinent wave function can be then used to describe its motion or to calculate the probability of tunneling through the energetic barrier, e.g. by means of the WKB (Wentzel-Kramers-Brillouin) approximation.

This behavior enables to use the following idea about the nature of activated complex (**Figure 7(a)**³²). The activated complex is in equilibrium with products ($K^\#$, please refer to the discussion of Eq. 5 in Chapter 2). The projection of this equilibrium is the linear spring, where the activated complex oscillates ($\pm r$) around the equilibrium position (please refer to note (4) and the discussion of Eq. 82). This oscillation is the characteristics symptom of negative feedback of activated complex to the products. Furthermore, the shift from the equilibrium position reduces the kinetic energy and increases the potential energy of activated complex.

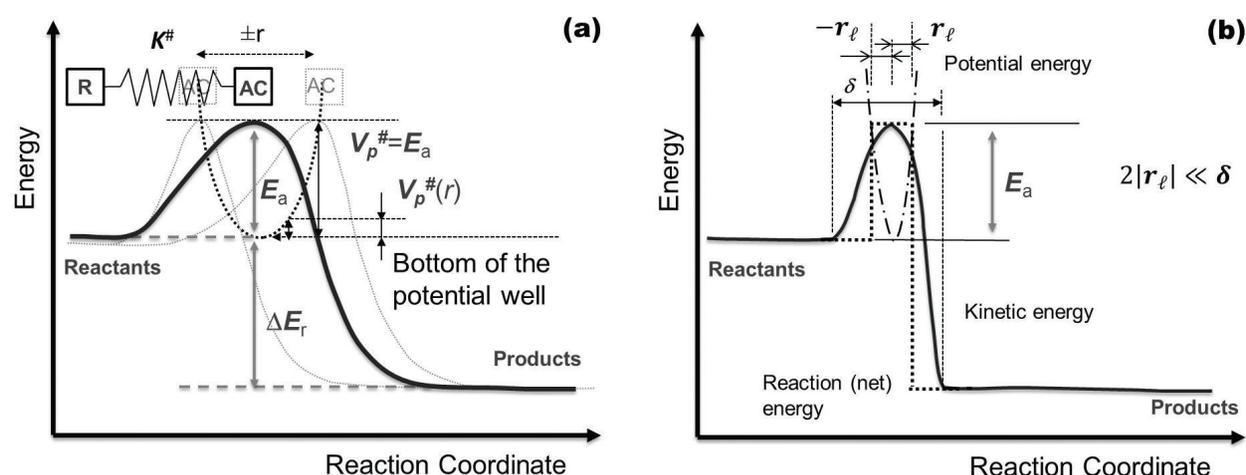


Figure 7. Simplified scheme of energy diagram (general exothermic reaction, please refer to **Figure 1(a)** in Chapter 2) showing increasing potential energy of activated complex (AC) caused by its oscillation around the peak of energetic barrier. The equilibrium of activated complex with reactants (**R**) was approximated by Hooke's spring (a). The scheme of energy diagram that includes the oscillation of activated state around the equilibrium position (b).

³²For the peak of energetic barrier, it can then be written:

$$E_r = \Delta E_r + E_a = \Delta E_r + \frac{\hbar^2 \bar{k}^2}{2 m_{(1)}^\#}; \quad (a)$$

that is, the relation which is analogical to the highest energies of the valence band and the lowest energies of the conduction band in many semiconductors:

$$E(\bar{k}) = E_0 + \frac{\hbar^2 \bar{k}^2}{2 m^*}; \quad (b)$$

where $E(\bar{k})$ is the energy of electron with the wave vector \bar{k} , E_0 is the edge of energy of band and m^* is the effective mass of electron.

This behavior of activated state attached by spring to the product can be approximated by the Hooke's law³³ [34, 35], where the force F , which shifts the activated complex from the peak of energetic barrier³⁴ is given by the Newton's second law⁴⁰:

$$F = -k_s^\# r = m_{(1)}^\# \frac{\partial^2 r}{\partial t^2} = m_{(1)}^\# a^\# \quad (113)$$

where $a^\#$ is the acceleration of activated molecule (Eq. 116) and $k_s^\#$ is the positive constant of the spring, which can be calculated from its angular frequency:

$$\omega^\# = \sqrt{\frac{k_s^\#}{m_{(1)}^\#}} \Rightarrow \omega^{\#2} = \frac{k_s^\#}{m_{(1)}^\#}. \quad (114)$$

That also means that the universal frequency of activated state ($\nu_{AC}^\#$) is independent of r ³⁵, that is it depends on the mass of activated complex only:

$$\nu_{AC}^\# = \frac{k_B T'}{h} = \frac{E_{(1)}}{h} = \frac{1}{2\pi} \sqrt{\frac{k_s^\#}{m_{(1)}^\#}} = \frac{1}{2\pi} \omega^\# \Rightarrow \quad (115)$$

$$E_{(1)} = \frac{h}{2\pi} \omega^\# = \hbar \omega^\# = k_B T'$$

The acceleration of activated molecule during this oscillation is then given by the formula:

$$a^\# = -\omega^{\#2} r = -4\pi^2 \nu_{AC}^{\#2} r. \quad (116)$$

The potential energy, which is stored in the spring (activated complex) during the oscillation, is given by the relation:

$$V_{p,1}^\#(r, t) = \frac{1}{2} k_s^\# r^2. \quad (117)$$

This behavior is in agreement with previous conclusions derived from Eq. 82. Since the change in the potential energy is of constant rate, the relation can also be written:

$$\frac{\partial^2 V_{p,1}^\#(r, t)}{\partial r^2} = k_s^\#. \quad (118)$$

The increase of energy (Eq. 117) then leads to the decrease of the momentum of activated complex (Eq. 111):

³³ English natural philosopher, architect and polymath Robert Hooke (1635–1703).

³⁴ The other end of spring, that is, the reactants, is considered for the fixed position.

³⁵ The net energy of the activated complex is constant during the time.

$$\bar{p}_{(1)}^{\#}(r, t) = \pm \sqrt{2m_{(1)}^{\#} (E_{(1)} - V_{p,1}^{\#}(r, t))} = \pm \sqrt{2m_{(1)}^{\#} (T_{(1)}^{\#}(r, t))} \quad (119)$$

where $T_{(1)}^{\#}(r, t)$ is the kinetic energy of activated complex during its oscillation around the energetic peak, so:

$$E_{(1)} = \frac{\bar{p}_{(1)}^{\#}(r, t)^2}{2m_{(1)}^{\#}} + V_{p,1}^{\#}(r, t). \quad (120)$$

Therefore, the momentum of activated complex is equal to zero when $E_{(1)} = V_{p,1}^{\#}$ (Figure 7(b)), that is for two spring limits, that is in amplitude positions:

$$r_{\ell} = \sqrt{\frac{2E_{(1)}}{k_s^{\#}}} = \frac{\lambda^{\#}}{\pi} = A_p \quad (121)$$

where $\lambda^{\#}/r_{\ell} = \pi$. Since there are no losses in the energy (the activated complex is an adiabatic system³⁶), the activation energy has a constant value of:

$$E_{(1)} = \frac{1}{2}k_s^{\#}r_{\ell}^2 = \frac{1}{2}m_{(1)}^{\#}\bar{v}^2. \quad (122)$$

Furthermore the value of $2|r_{\ell}| \ll \delta$ is very small in comparison to the length of potential barrier (Eq. 54). In other words, the length of energetic barrier is much longer than the section which belongs to the oscillation of activated complex. The pertinent wave can then be described by the equation for the simple harmonic motion:

$$r(t) = A_p \cos(2\pi\nu_{AC}^{\#}t) \quad (123)$$

where $A_p = r_{\ell}$ (Eq. 121) is the amplitude and $\nu_{AC}^{\#}$ is the universal frequency of activated complex (Eq. 115). Further treatment of Eq. 123 then leads to the formula of the wave function³⁷:

$$r(t) = \sqrt{\frac{2E_{(1)}}{k_s^{\#}}} \cos\left(\sqrt{\frac{k_s^{\#}}{m_{(1)}^{\#}}}t\right) = \frac{\lambda^{\#}}{\pi} \cos\left(\sqrt{\frac{k_s^{\#}}{m_{(1)}^{\#}}}t\right) \quad (124)$$

and then:

³⁶The "walls" of this system do not allow the transport of matter and heat.

³⁷The formula is the solution of an ordinary differential equation (ODE):

$$m_{(1)}^{\#} \frac{\partial^2 r}{\partial t^2} + k_s^{\#} r = 0 \implies m_{(1)}^{\#} \frac{\partial^2 r}{\partial t^2} = -k_s^{\#} r.$$

Please refer also to Eq. 13 in Chapter 2.

$$r(t) = \frac{\lambda^\#}{\pi} \cos \left(\sqrt{\frac{k_s^\#}{m_{(1)}^\#}} t \right) = \frac{\lambda^\#}{\cos^{-1}(-1)} \cos \left(\sqrt{\frac{k_s^\#}{m_{(1)}^\#}} t \right) \quad (125)$$

$$\cong \frac{\lambda^\#}{0.31831} \cos \left(\sqrt{\frac{k_s^\#}{m_{(1)}^\#}} t \right)$$

Since the magnitude of this function starts with the value $r(0) = r_\ell$, it is possible to shift the beginning of wave function (negative phase shift about $-\pi/2 = -1.570796$ radians^{38,39}) to the peak of energetic barrier, where $r(0) = 0$, then the wave function can be written:

$$r(t) = \sqrt{\frac{2E_{(1)}}{k_s^\#}} \cos \left(\left(\sqrt{\frac{k_s^\#}{m_{(1)}^\#}} t \right) - \frac{\pi}{2} \right) = \frac{\lambda^\#}{\pi} \sin \left(\sqrt{\frac{k_s^\#}{m_{(1)}^\#}} t \right) \quad (126)$$

The period of this equation is given by the relation:

$$T^\# = 2\pi \sqrt{\frac{m_{(1)}^\#}{k_s^\#}} \quad (127)$$

This solution also provides an important insight to the nature of the mass and the velocity vector of activated state, which can be actually characterized as follows:

- Reduced (effective³²) mass of activated state ($m_{(1)}^\#$);
- Relative velocity of the bodies before the collision (\bar{v}).

The activation can then be characterized as the change in kinetic energy during the perfectly elastic collision. Since there is no dissipation, if the kinetic energy is dissipated (the formation of activated state is a reversible process), the change of energy for this kind of collisions is:

³⁸Like e and π , the $\pi/2$ is the transcendental number. This value corresponds to 90° , i.e. to 1 quadrant. The positive phase shift about $3\pi/2 = 4.712388\dots$ radians, i.e. 270° (3 quadrants), which leads to the equation:

$$r(t) = \sqrt{\frac{2E_{(1)}}{k_s^\#}} \cos \left(\left(\sqrt{\frac{k_s^\#}{m_{(1)}^\#}} t \right) + \frac{3\pi}{2} \right) = \frac{\lambda^\#}{\pi} \sin \left(\sqrt{\frac{k_s^\#}{m_{(1)}^\#}} t \right); \quad (a)$$

has the same effect, because:

$$\cos \left(x - \frac{\pi}{2} \right) = \cos \left(x + \frac{3\pi}{2} \right) = \sin(x). \quad (b)$$

³⁹There is a very important fact that this phase shift corresponds to complete elliptic integral of the second kind:

$$\frac{\pi}{2} = E(0);$$

especially for the investigation of kinetics of thermal decomposition of solids by TA methods¹, but we will deal with the details of this topic in future article.

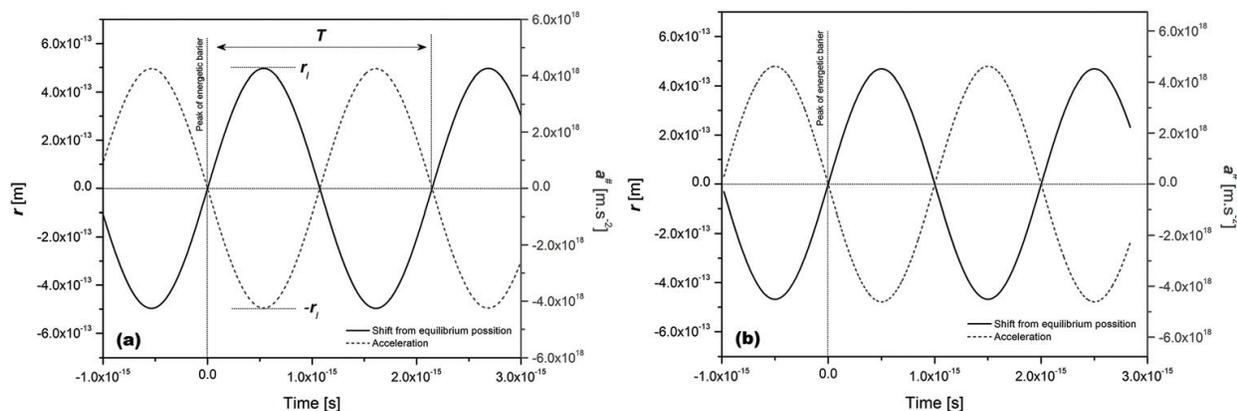


Figure 8. The wave function (Eq. 115) of activated state for the thermal decomposition of calcite (a) and aragonite (b).

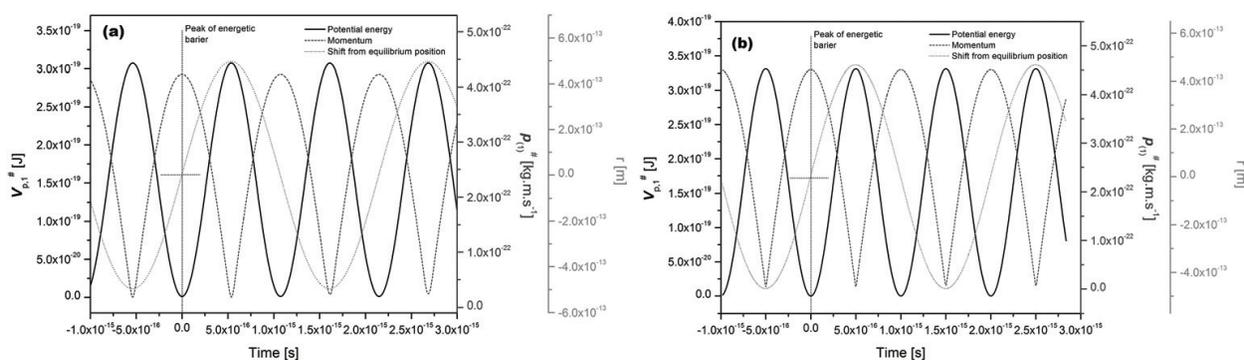


Figure 9. The change of potential energy and of momentum during the oscillation of activated complex during the process of thermal decomposition of calcite (a) and aragonite (b).

$$E_{(1)} = \frac{1}{2} m_{(1)}^{\#} \bar{v}^2 (\varphi^2 - 1) \quad (128)$$

where $\varphi = \sqrt{E_{(1)}/E_{(i,1)}} = 1$ (elastic collision) is the coefficient of restitution (COR). Its value is defined as the ratio of the final to initial relative velocity or the square root ratio of the final ($E_{(1)}$) to initial energy ($E_{(i,1)}$) of two collided objects⁴⁰.

The graphs of the wave function for the process of thermal decomposition of calcite (a) and aragonite (b) are shown in **Figure 8**. It can be seen that calcite with lower activation energy (**Table 1** and **Table 2**) has longer period ($2.15 \cdot 10^{-15} \text{ s}^{-1}$) than aragonite ($2.0 \cdot 10^{-15} \text{ s}^{-1}$). Furthermore, the wavelength is then only a tiny quantity of length of the energetic barrier (**Figure 7(a)**).

The changes of the potential energy and of momentum of activated complex during the oscillation around the equilibrium position, that is the peak of energetic barrier ($r = 0$), is shown in **Figure 9**.

⁴⁰From this point of view, please see also the text (Van't Hoff statement) related to the discussion of Eq. 9 in Chapter 1.

The wave function (Eqs. 113 and 114) can also be approximated by the Taylor (Maclaurin, please refer to footnote 15 in Chapter 2) series expansion around the point $r(0)$ ⁴¹:

$$r(0) = \frac{\lambda^\#}{\pi} \left(1 - \frac{x^2}{2} + \frac{x^4}{24} - \frac{x^6}{720} \dots \right) \cong \frac{\lambda^\#}{\pi}; \text{ where } x = \sqrt{\frac{k_s^\#}{m_{(1)}^\#}} t. \quad (129)$$

For Eq. 126 (or Equation in Footnote 40) with the phase shift to the peak of energetic barrier, it is possible to write:

$$r(0) = \frac{\lambda^\#}{\pi} \left(x - \frac{x^3}{6} + \frac{x^5}{120} - \frac{x^7}{5440} \dots \right) = \frac{\sqrt{2E_{(1)}}}{\sqrt{k_s^\#}} \left(x - \frac{x^3}{6} + \frac{x^5}{120} - \frac{x^7}{5440} \dots \right) \quad (130)$$

Furthermore, it is also obvious (please refer to Eqs. 121–125) that:

$$E_{(1)} = \frac{1}{2} k_s^\# \left(\frac{\lambda^\#}{\pi} \right)^2 = \frac{1}{2} m_{(1)}^\# \bar{v}^2 \quad (131)$$

that is:

$$k_s^\# \left(\frac{\lambda^\#}{\pi} \right)^2 = m_{(1)}^\# \bar{v}^2 = \frac{\bar{p}_{(1)}^\# 2}{m_{(1)}^\#} = 2E_{(1)} \quad (132)$$

where:

$$k_s^\# = m_{(1)}^\# \left(\frac{\bar{v} \pi}{\lambda^\#} \right)^2 \quad \left[\frac{kg}{s^2} = \frac{N}{m} \right]. \quad (133)$$

Since the activation energy per one activated complex is the sum of its kinetic ($E_{(k,1)}$) and potential energy ($V_{p,1}^\#$):

⁴¹Since:

$$f(x) = \cos(x) \implies f(0) = 1; \quad (a)$$

$$f'(x) = -\sin(x) \implies f'(0) = 0; \quad (b)$$

$$f''(x) = -\cos(x) \implies f''(0) = -1; \quad (c)$$

$$f'''(x) = \sin(x) \implies f'''(0) = 0, \text{ etc.}; \quad (d)$$

the substitution to Eq. (a) in footnote 60 provides the series expansion according to Eq. 129.

$$E_{(1)} = E_{(k,1)} + V_{p,1}^{\#} \quad (134)$$

it can be written⁴²:

$$E_{(1)} = \frac{1}{2} m_{(1)}^{\#} \omega^{\#2} A_p^2 \cos^2(\omega^{\#} t) + \frac{1}{2} k_s^{\#} A_p^2 \sin^2(\omega^{\#} t). \quad (135)$$

Because the frequency of $E_{(k,1)}$ and $V_{(p,1)}^{\#}$ is twice as high as the frequency of oscillation⁴³, the middle (average) potential ($V_{(p,1,av)}^{\#}$) and the kinetic energy ($E_{(k,1,av)}$) are of the same size during all periods. So, the relation of the middle activation energy ($E_{(1,av)}$) of the reaction can be written as follows:

$$E_{(1,av)} = E_{(k,1,av)} = V_{(p,1,av)}^{\#} = \frac{1}{4} k_s^{\#} A_p^2 = \frac{E_{(1)}}{2}. \quad (136)$$

The value of “effective” shift (r_{ef}) where the energy that corresponds to the value of $E_{(1,av)}$ is reached, can be then calculated as follows (please refer to Eqs. (70) and (121)):

$$r_{ef} = \frac{1}{\sqrt{2}} A_p = 0.707 \dots r_{\ell} = \frac{r_{\ell}}{\sqrt{2}} = \frac{\bar{v}_x r_{\ell}}{\bar{v}}. \quad (137)$$

With respect to Eqs. (59) and (62), the relation can also be written:

$$\frac{E_{(1)}}{E_{(1,av)}} = \frac{\Delta H^{\#}}{\Delta U^{\#}} = \frac{K_B}{p} = 2. \quad (138)$$

Eq. 115 enables to use the principle of equivalency between undamped (the damping factor or ratio $\zeta = 0$) harmonics oscillators (universal oscillator equation) in order to imagine or simulate the behavior of activated state as a serial RCL (Resistor, Inductor and Capacitor) or parallel RCL circuit:

$$v^{\#} = \frac{1}{2\pi} \sqrt{\frac{k_s^{\#}}{m_{(1)}^{\#}}} = \frac{1}{2\pi} \sqrt{\frac{1}{LC}}. \quad (139)$$

In the series RCL circuit the inductance L is equal to the mass of activated molecule $m_{(1)}^{\#}$ and the elastnace $1/C$ corresponds to the spring constant $k_s^{\#}$. In the case of parallel RCL circuit the value of $k_s^{\#}$ is equal to the magnetic reluctance $1/L$ and $m_{(1)}^{\#}$ to the capacitance C .

If we conceive the idea that these oscillating systems are actually not undamped, but very slightly underdamped (factor $\zeta < < 1$), there is an option to explain the decomposition of activated state, by the exponential decay of angular frequency and then by the energy (Eq. 115) of oscillator. That means that the energy of activated complex is not sufficient to

⁴²In the case that there is not any phase shift.

⁴³Please refer also to Eq. 115 and to **Figure 9**.

overcome the peak of energetic barrier at certain time after its formation. Depending on actual position on reaction coordinate ($r(t)$, refer to Eq. 124), the activated complex is decomposed into products or into reactants.

Since the rate of reaction is proportional to the decomposition of activated state, it should be proportional to the damping ratio as well. Therefore, the following approximation between the rate constant of reaction (k) and dimensionless damping factor can be suggested:

$$k(T) = \zeta(T) \omega^\# = \zeta(T) \sqrt{\frac{k_s^\#}{m_{(1)}^\#}} \quad (140)$$

In other words, the exponential decay of underdamped oscillator is equal to k , that is the mean lifetime ($\tau = 1/k$) of activated complex decreases with temperature, while the value of damping factor increases with temperature. The rate of reaction then becomes faster. The substitution of Arrhenius formula (Eq. 7 in Chapter 1) to Eq. 140 then leads to the relation:

$$k_s^\# = m_{(1)}^\# \left(A \exp\left(-\frac{E_a}{RT}\right) / \zeta(T) \right)^2 = m_{(1)}^\# \left(\frac{k(T)}{\zeta(T)} \right)^2 \quad (141)$$

The value of so called Q factor of activated complex can then be calculated from the following relation:

$$Q = 2\pi \frac{\text{Energy stored}}{\text{Energy lost}} = \frac{2\pi E_{(1)}}{\text{Energy lost}} = \frac{1}{2\zeta(T)} \quad (142)$$

Using the example of the process of thermal decomposition of aragonite applied in this book, the lost energy can be calculated (Eq. 142) to 8.622×10^{-37} J per one cycle of activated molecule, which is only very tiny fraction of its value.

Since the loss of energy per each cycle increases with the energy of the activation impulse, the same idea can be used to explain the decomposition of activated system which collects the energy $E \geq E_a$. In other words, if tunneling (please refer to Section 5 in Chapter 2) is not taken into account, the energetic barrier behaves as an energy filter which allows only to the activated molecule with the energy of E_a to pass through (to form the product). The systems with higher or lower energy are not allowed to go through the energetic barrier. The system with higher energy oscillates and loses its energy until it reaches the activation energy E_a and in this stage it passes through. The condition must always be fulfilled that the net energy is the sum of activation energy and of the energy of reaction, that is $\Delta E_r + E_a$ (please see **Figure 7**).

5. Other parameters that affect the effective mass of activated state

As results from previous discussion, the effective mass as well as other derived parameters of activated complex are independent of the temperature at which the reaction proceeds at

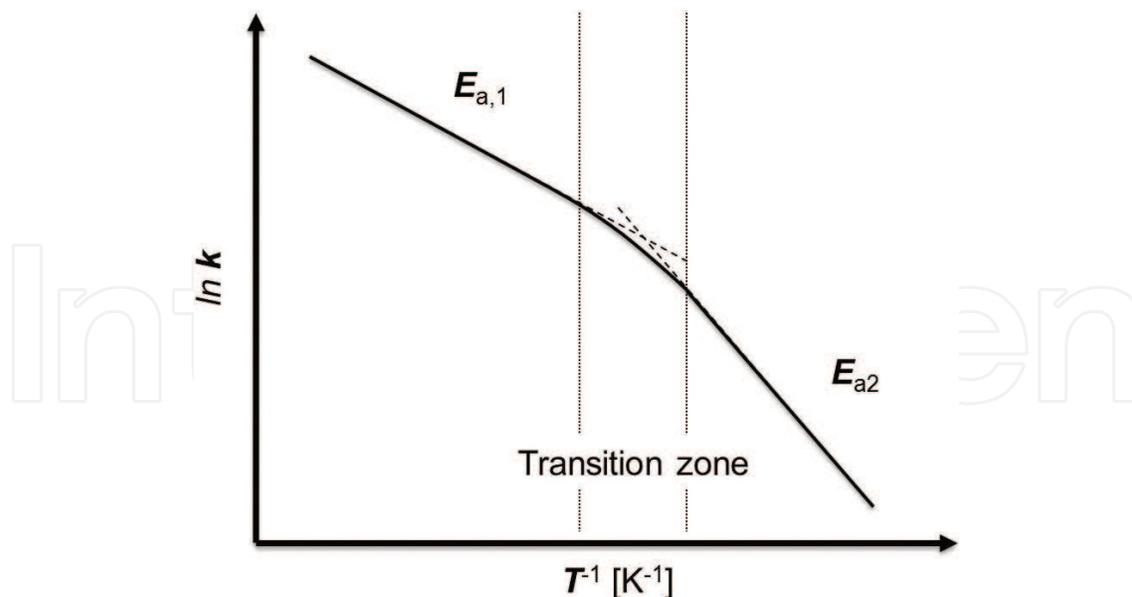


Figure 10. Hypothetical example of Arrhenius plot for the change of reaction mechanism with increasing temperature.

measurable rate⁴⁴. Of course, that is possible only on the assumption that the change in temperature does not bring the change of reaction mechanism with different activation energy⁴⁵ (**Figure 10**). In that case, the activation energy, the mass of activated state as well as other above mentioned parameters of activated complex must be changed too. The example of that behavior can be found in previous works, e.g. [36, 37].

Since the effective mass of activated state could also be affected by the isotopic composition of the specimen (please refer to Section 5 in Chapter 2), the activation energy for the most cases of the process is actually Relative Activation Energy. The value of which depends on the isotopic composition of the sample. Please do not be confused with the apparent activation energy. This term is usually applied to the kinetics of processes of unknown or uncertain mechanism.

⁴⁴On assumption that the activation energy is independent of the temperature. As was firstly assumed by van't Hoff (please refer to discussion of Eq. 18 in Chapter 1), the activation energy could be a function of temperature. From this point of view, please refer also to the work of S. Vyazovkin and B.V. L'vov. Also according to our investigation, the activation energy is most probably the function of temperature, but within the temperature interval, where the reaction takes place in measurable rate, this change is usually smaller than the uncertainty of experimental results. We plan to publish our solutions on this topic in the future work.

⁴⁵In this case, we can observe two or more linear parts in Arrhenius plot which are pertinent to the change of reaction mechanism. The mechanism crossing is usually gradual without an abrupt change of the slope. The effect of temperature on the reaction mechanism can be, for example, illustrated by the effect of temperature on the process of nucleation and diffusion. The increasing temperature makes the transport phenomenon's, for example, the diffusion toward growing nucleus of new phase, easier, but it also reduces overcooling, for example, driving force of nucleation, as well.

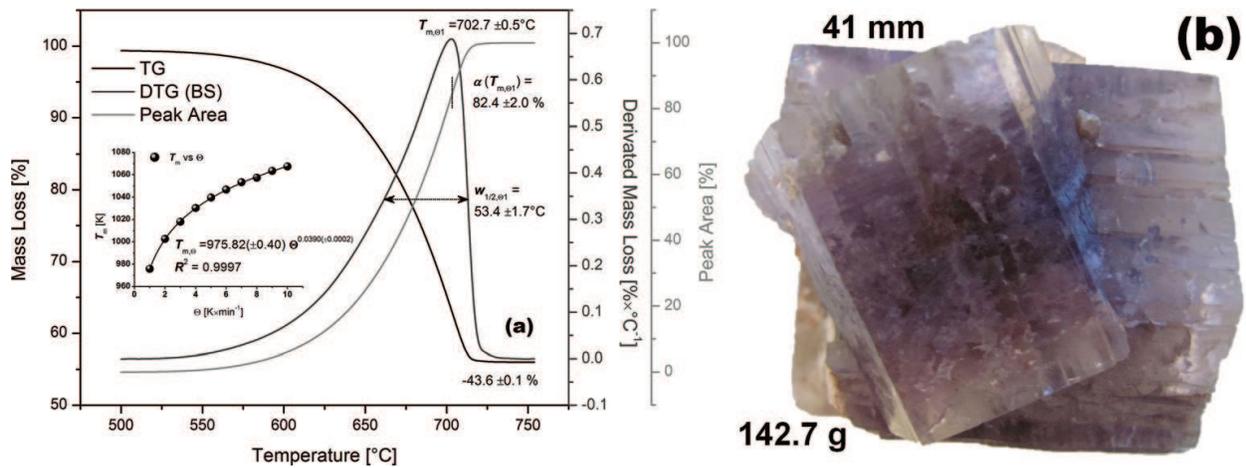


Figure 11. Thermal decomposition of aragonite (20 mg) heated with the rate of $1 \text{ K}\cdot\text{min}^{-1}$ under inert (N_2) atmosphere (a). DTG peak was subtracted to baseline (BS). The plot of T_m vs. Θ is shown in detail. Photograph of analyzed pseudo-hexagonal (violet crystals show a hexagonal outline) aragonite specimen (b).

The change in mass when reactants pass into the activated state is also affected by polymorphism⁴⁶, that is by the crystal structure. For example, the aragonite has higher $M^\#$ than calcite, despite the fact that both minerals have the same chemical composition (CaCO_3), so their thermal decomposition can be described by the same chemical equation (Eq. 33 in Chapter 2).

The course of thermal decomposition of aragonite specimen (La Pesquera, Spain) is shown in **Figure 11**. In comparison with the process of thermal decomposition of calcite (**Figure 1**), the peak temperature of the process is higher. On the contrary, the full width at half maximum of peak ($w_{1/2}$) is lower for aragonite than for calcite.

The Arrhenius plot for the process of thermal decomposition of aragonite⁴⁷ is shown in **Figure 12**. The process of thermal decomposition of aragonite requires slightly higher activation energy (**Table 2**) than that of Iceland spar (**Table 1**). The mechanism of the process of thermal decomposition, which includes zero or decreasing nucleation rate of new phase and the diffusion controlled growth of new phase, is also very similar for calcite and aragonite. Please compare the data in **Table 1** (calcite) with those in **Table 2** (aragonite) for the demonstration of effect of polymorphism on the kinetics of thermal decomposition and properties of activated complex. Further research has shown that there is actually not any significant effect of the polymorphism of calcium carbonate⁴⁸ or its origin on the value of activation energy for the specimens of comparable purity [38].

⁴⁶Polymorphism is the ability of solids to crystallize in various structures in different intervals of temperature and pressure. In the case of chemical elements, the same ability is termed as allotropism (allotropy). For example, the calcite and aragonite are two polymorphs of CaCO_3 and graphite and diamond are two of allotropes of carbon.

⁴⁷The chemical equation is the same as for calcite (Eq. 33 in Chapter 2). The Arrhenius and Eyring plot for the process of thermal decomposition of calcite can be found in Figure 2 in Chapter 2.

⁴⁸This behavior can be explained by very small value of enthalpy of calcite (trigonal) \leftrightarrow aragonite (orthorhombic) phase transition (please refer also to the footnotes 18 and 19 in Chapter 2). The same cannot be said for vaterite, but this phase is the synthetic hexagonal calcium carbonate polymorph, that is, vaterite cannot be classified as a mineral.

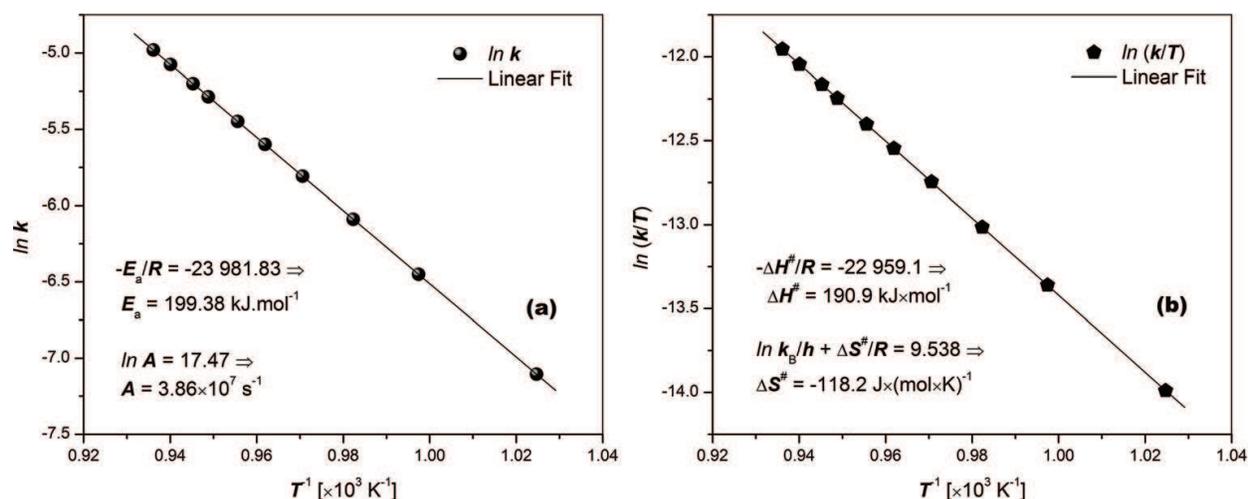


Figure 12. Arrhenius plot (a) and Eyring plot (b) for the process of thermal decomposition of aragonite.

The same cannot be recognized for polymorphs of SrCO_3 , which was investigated in previous work [39]. The mass of activated state is higher for orthorhombic polymorph ($0.165 \text{ kg.mol}^{-1}$) than for hexagonal ($0.148 \text{ kg.mol}^{-1}$) strontium carbonate, but the effect of temperature change on the mechanism, that is the value of kinetic exponent n , of thermal decomposition was included in this particular case. Furthermore, the kinetics of the thermal decomposition process and then the effective mass of activated state as well could be influenced by the formation of solid solution.

6. Conclusion

As was demonstrated in this chapter, the effective (reduced) mass of activated state is an important parameter of activated complex, which can be easily derived from the results of kinetic experiments. As was demonstrated on the example of calcite and aragonite, this change in mass when reactants pass into an activated state depends on real reaction mechanism, resp. on kinetic factor, which is often different from common transcript of the reaction. Therefore, the mass of activated state could be different from the value resulting from this equation, that is the sum of reactants multiplied by their stoichiometric coefficients.

The most important significance of this parameter lays also in the possibility of further definition of rate, density, energetic density, current mass density, momentum and many other properties of activated complex. Since the activation energy and the momentum of activated complex enable complete characterization of the motion of activated complex alongside the reaction coordinate, these parameters are its quantum numbers.

Furthermore, it is possible to introduce the idea to approximate the behavior of activated complex by the spring oscillation and to determine the nature of mass of activated complex as the reduced or effective mass of activated complex. This mass is also affected by the isotopic composition of the sample and by polymorphism.

Symbols and abbreviations

The following abbreviations and symbols are used in this book:

$\vec{j}^\#$	mass flux (mass current density) of activated complex
\bar{v}_p	the speed of the phase wave (phase velocity)
\bar{v}_x	the effective speed of activated complex, which corresponds to the scale parameter of Maxwell–Boltzmann distribution
$\Delta_r G^\circ$	standard Gibbs free energy of the reaction
$\Delta_r G$	Gibbs free energy of the reaction
$\Delta G^\#$	Gibbs energy of activation
$\Delta H^\#$	enthalpy of activation
$\Delta S^\#$	entropy of activation
$\Delta U^\#$	internal energy of activation
$\Delta V^\#$	volume of activation, the change of volume when reactants pass into the activated state
$B_{av}(x)$	the average value of approximation parameter $B(x)$
C_{PA}	Plouffe's constants
C_{PT}	Pythagorean triple constant for hypotenuses
$E_{(i,1)}$	initial energy of two collided object
E_0	energetic difference between energy of activated state and reactants
E_a	activation energy (Arrhenius activation energy)
E_p	Planck energy ($1.956 \cdot 10^9$ J)
E_{th}	activation energy (theoretically calculated)
\hat{H}	Hamiltonian (Evolutional) operator
$K^\#$	equilibrium constant (formation of activated complex)
K^+	equilibrium constant of activation ($K^\# = K^+$)
K_b	the bulk modulus
L_p	Planck length ($1.616 \cdot 10^{-35}$ m)
$M^\#$	the mass of activated state
M_a	Mach number

N_A	Avogadro constant ($6.022140857 \cdot 10^{-23} \text{ mol}^{-1}$)
$Q_0^\#$	partition function of activated complex
Q_i	partition function of reactant molecules
$T^\#$	period of activated complex wave function
\hat{T}	kinetic energy operator
T'	activated complex temperature term (E_a/R)
$V^\#$	molar volume of activated state ($V^\# = RT'/p$)
\hat{V}	potential energy operator
$V_{p,1}^\#$	potential energy of activated complex
Z_p	the size of particle
$a^\#$	acceleration of activated molecule
g_j	degeneracy factor, that is the number of allowed equimolar quantum microstates
$k^\#$	activated state rate constant (coefficient)
\bar{k}	wave vector
k_B	Boltzmann constant ($1.38064852 \cdot 10^{-23} \text{ J} \cdot \text{K}^{-1}$)
k_{exp}	rate constant (experimentally determined)
k_{th}	rate constant (theoretically calculated)
$m_{(1)}^{\#,0}$	the invariant mass of activated complex
\bar{p}	momentum
$r^\#$	specific gas constant
\bar{r}	position vector
$r_{AC}^\#$	the effective diameter of activated complex
$t_{1/2}$	the half-life of activated complex
t_p	Planck time ($5.391 \cdot 10^{-44} \text{ s}$)
$t_\delta = 1/A$	the mean lifetime of activated complex, that is the time required to overcome energetic barrier
\bar{v}	the most probable speed of activated complex (the mode of Maxwell-Boltzmann distribution), which corresponds to the group velocity of the activation wave

$w_{1/2}$	full width at half maximum of peak (FWHM)
α_{Q^\ddagger}	coefficient of response of partition function to a change in temperature
β_v	dimensionless rate ratio of activated complex to the speed of light
ϵ_j	energy level of j -microstate
λ^\ddagger	de Broglie wavelength of activated complex
ν^\ddagger	universal frequency ($\nu^\ddagger = (k_B T)/h$), that is the frequency of decomposition of activated complex
ν_{AC}^\ddagger	universal frequency of activated complex ($\nu_{AC}^\ddagger = (k_B T)/h$)
ν_i	stoichiometric coefficients
ρ^\ddagger	density of activated state
ρ_{sf}	steric factor
ω^\ddagger	angular frequency of activated complex
$\Delta = \nabla^2$	Laplace operator (Laplacian)
\wp	coefficient of restitution (COR)
ΔV	molar change in volume during reaction
A	frequency or pre-exponential Factor, sometimes prefactor
A'	temperature independent constant
AC	activated complex
ART	Absolute reaction rates theory
$B(x)$	approximation parameter in the Doyle equation for $\mathbf{p}(\mathbf{x})$
E	energy, usually reaction energy
F	force
G	gravitational constant (Universal constant or Newton's constant, $6.67408 \times 10^{-11} \text{ m}^3 \cdot \text{kg}^{-1} \cdot \text{s}^{-2}$)
K	equilibrium constant of reaction
P	Ad hoc quantity, that is "fudge factor"
Q	partition function of the molecule and Q factor
R	Gas constant, also Molar, Universal or Ideal gas constant ($8.3144598 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$)

S	entropy
STR	Special theory of relativity
T	thermodynamic or absolute temperature
TST	Transition state theory
W	energetic difference between reactants and activated complex in basic state
Y	the constant term ($Y \approx 7.0383 \times 10^{-45} m^5/s^3$)
c	speed of light in vacuum ($299,792,458 \text{ m}\cdot\text{s}^{-1}$)
$const.$	square of temperature-rate kinetic coefficient
$const.$	temperature-rate kinetic coefficient
e	the base of natural logarithms (Euler's number, Napier's constant)
h	Planck constant ($6.626070040 \times 10^{-34} \text{ J}\cdot\text{s}$)
k	reaction rate constant (coefficient)
m	mass
p	pressure
$p(x)$	temperature integral, where the quantity of $x = E_a/RT$
q	the heat of reaction
r	reaction rate (rate or speed of reaction) or shift from equilibrium position (according to the context)
Θ	heating rate
∇	Nabla (del) operator
β	thermodynamic beta (occasionally perk)
γ	Lorentz factor (term)
δ	the length of energetic barrier
κ	proportionality constant (transmission coefficient)
ν	frequency of harmonic oscillator
o	energy ratio
ς	damping factor
τ	fundamental temperature
ψ	wave function (psi)
ϕ	potential force-field

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References

- [1] Truhlar DG, Garrett BC, Klippenstein SJ. Current status of transition-state theory. *The Journal of Physical Chemistry*. 1996;**100**(31):12771-12800. DOI: 10.1021/jp953748q
- [2] Ptáček P, Opravil T, Šoukal F. Introduction of novel kinetic approach to calculation of activation energy and its application to the sinter-crystallization of strontian feldspar. *Ceramics International*. 2016;**42**(15):16969-16980. DOI: 10.1016/j.ceramint.2016.07.203
- [3] Lever T, Haines P, Rouquerol J, Charsley EL, Van Eckeren P, Burlett DJ. ICTAC nomenclature of thermal analysis (IUPAC recommendations 2014). *Pure and Applied Chemistry*. 2014;**86**(4):545-553. DOI: 10.1515/pac-2012-0609
- [4] Kostyrko K, Skoczylas M, Klee A. Certified reference materials for thermal analysis. *Journal of Thermal Analysis*. 1988;**33**(1):351-357. DOI: 10.1007/BF01914623
- [5] Andon RJL, Connett JE. Calibrants for thermal analysis. Measurement of their enthalpies of fusion by adiabatic calorimetry. *Thermochimica Acta*. 1980;**42**(2):241-247. DOI: 10.1016/0040-6031(80)87106-1
- [6] Robbins SA, Rupard RG, Weddle BJ, Maull TR, Gallagher PK. Some observations on the use of strontium carbonate as a temperature standard for DTA. *Thermochimica Acta*. 1995;**269-270**:43-49. DOI: 10.1016/0040-6031(95)02602-9
- [7] Šesták J, Hubík P, Mareš JJ. Thermal physics and thermal analysis: From macro to micro, highlighting thermodynamics, kinetics and nanomaterials. *Hot topics in thermal analysis and calorimetry*. Springer. 2017;**11**:567 p. DOI: 10.1007/978-3-319-45899-1
- [8] Augis JA, Bennett JE. Calculation of the Avrami parameters for heterogeneous solid state reaction using a modification of the Kissinger method. *Journal of Thermal Analysis*. 1978;**13**(2):283-292. DOI: 10.1007/BF01912301
- [9] Avrami M. Kinetics of phase change. I. General theory. *Journal of Chemical Physics*. 1939;**7**(12):1103-1112. DOI: 10.1063/1.1750380
- [10] Avrami M. Kinetics of phase change. II. Transformation-time relations for random distribution of nuclei. *Journal of Chemical Physics*. 1940;**8**(2):212-224. DOI: 10.1063/1.1750631
- [11] Kolmogorov AN. A statistical theory for the recrystallization of metals. *Izvestiya Akademii Nauk SSSR, Ser. Math.* 1937;**1**(3):355-359

- [12] Johnson WA, Mehl RF. Reaction kinetics in processes of nucleation and growth. *Transactions of the American Institute of Mining & Metallurgical Engineers*. 1939;**135**:416-458. DOI: 10.1007/s11661-010-0421-1
- [13] Christian JW. *The Theory of Transformations in Metals and Alloys*. 2nd ed. New York: Pergamon Press; 1975. 586 p
- [14] Kissinger HE. Reaction kinetics in differential thermal analysis. *Analytical Chemistry*. 1957;**29**(11):1702-1706. DOI: 10.1021/ac60131a045
- [15] Ptáček P, Frajkorová F, Šoukal F, Opravil T. Kinetics and mechanism of three stages of thermal transformation of kaolinite to Metakaolinite. *Powder Technology*. 2014;**264**:439-445. DOI: 10.1016/j.powtec.2014.05.047
- [16] Doyle CD. Estimating isothermal life from thermogravimetric data. *Journal of Applied Polymer Science*. 1962;**6**(24):639-642. DOI: 10.1002/app.1962.070062406
- [17] Lyon RE. An integral method of nonisothermal kinetic analysis. *Thermochimica Acta*. 1997;**297**(1-2):117-124. DOI: 10.1016/S0040-6031(97)00158-5
- [18] Mallakpour S, Taghavi M. The accuracy of approximation equations in the study of thermal decomposition behaviour of some synthesized optically active polyamides. *Iranian Polymer Journal*. 2009;**18**(11):857-872
- [19] Flynn JH, Wall LA. General treatment of the Thermogravimetry of polymers. *Journal of Research of the National Bureau of Standards-A, Physics and Chemistry*. 1966;**70A**(6):487-523. DOI: 10.6028/jres.070A.043
- [20] Coats AW, Redfern JP. Kinetic parameters from thermogravimetric data. *Nature*. 1964;**201**(4914):68-69. DOI: 10.1038/201068a0
- [21] Balarin M. Improved approximations of the exponential integral in tempering kinetics. *Journal of Thermal Analysis and Calorimetry*. 1977;**12**(2):169-177. DOI: 10.1007/BF01909473
- [22] Senum GI, Yang RT. Rational approximations of the integral of the Arrhenius function. *Journal of Thermal Analysis and Calorimetry*. 1977;**11**(3):445-447. DOI: 10.1007/BF01903696
- [23] Doyle CD. Kinetic analysis of thermogravimetric data. *Journal of Applied Polymer Science*. 1961;**5**(15):285-292. DOI: 10.1002/app.1961.070051506
- [24] Málek J. The shape of Thermoanalytical curves as a function of the reaction kinetics. *Thermochimica Acta*. 1993;**222**(1):105-113. DOI: 10.1016/0040-6031(93)80544-K
- [25] Gorbachev VM. Remarks on the application of the combined Kolmogorov - Erofeev - Kazeev - Avrami - Mampel equation in the kinetics of non-isothermal transformations. *Journal of Thermal Analysis and Calorimetry*. 1978;**13**(3). DOI: 509-514. DOI: 10.1007/BF01912390
- [26] Connors KA. *Chemical kinetics: The study of reaction rates in solution*. 2nd ed. John Wiley & Sons. 1990; 480 p.

- [27] Beruto D, Searcy AW. Use of the Langmuir method for kinetic studies of decomposition reactions: Calcite (CaCO_3). *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*. 1974;**70**:2145-2153. DOI: 10.1039/f19747002145
- [28] Maciejewski M. Computational aspects of kinetic analysis. Part B: The ICTAC kinetics project - the decomposition kinetics of calcium carbonate revisited, or some tips on survival in the kinetic minefield. *Thermochimica Acta*. 2000;**355**(1-2):145-154. DOI: 10.1016/S0040-6031(00)00444-5
- [29] L'vov BV, Polzik LK, Ugolkov VL. Decomposition kinetics of calcite: A new approach to the old problem. *Thermochimica Acta*. 2002;**390**(1-2):5-19. DOI: 10.1016/S0040-6031(02)00080-1
- [30] Navarro CR, Agudo ER, Luque A. Thermal decomposition of calcite: Mechanisms of formation and textural evolution of CaO nanocrystals. *American Mineralogist*. 2009; **94**(4):578-593. DOI: 10.2138/am.2009.3021
- [31] Halikia I, Zoumpoulakis L, Christodoulou E, Prattis D. Kinetic study of the thermal decomposition of calcium carbonate by isothermal methods of analysis. Technical Note. *The European Journal of Mineral Processing and Environmental Protection*. 2001;**1**(2):89-102. DOI: 10.1179/174328507X198591
- [32] Matvienko AA, Chizhik SA, Sidel'nikov AA. A new kinetic model of calcite thermal decomposition. *Doklady Physical Chemistry*. 2013;**451**(2):184-186 (Original Russian text published in *Doklady Akademii Nauk* 2013;**45**(6):647-649)
- [33] De Broglie L. Waves and quanta. *Nature*. 1923;**112**:540. DOI: 10.1038/112540a0
- [34] Hooke R. *Lectures de Potentia Restitutiva, Or of spring explaining the power of springing bodies*. London: John Martyn; 1678. 56 p
- [35] Roesler J, Harders H, Baeker M. *Mechanical Behaviour of Engineering Materials: Metals, Ceramics, Polymers, and Composites*. Springer Science & Business Media; 2007. 534 p
- [36] Ptáček P, Křečková M, Šoukal F, Opravil T, Havlica J, Brandštetr J. The kinetics and mechanism of kaolin powder sintering I. The Dilatometric CRH study of sinter-crystallization of Mullite and Cristobalite. *Powder Technology*. 2012;**232**:24-30. DOI: 10.1016/j.powtec.2012.07.060
- [37] Ptáček P, Šoukal F, Opravil T, Havlica J, Brandštetr J. Crystallization of spinel phase from Metakaoline: The nonisothermal Thermodilatometric CRH study. *Powder Technology*. 2013;**243**:40-45. DOI: 10.1016/j.powtec.2013.03.031
- [38] Ptáček P, Šoukal F, Opravil T. Kinetics and mechanism of thermal decomposition of calcite and aragonite. *Journal of Mineral, Metal and Material Engineering*. 2017;**3**:71-79
- [39] Ptáček P, Bartoníčková E, Švec J, Opravil T, Šoukal F, Frajkorová F. The kinetics and mechanism of thermal decomposition of SrCO_3 polymorphs. *Ceramics International*. 2015;**41**(1):115-126. DOI: 10.1016/j.ceramint.2014.08.043

