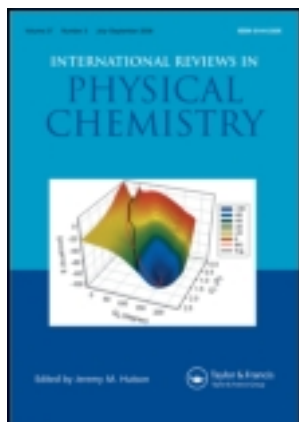


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Kinetic concepts of thermally stimulated reactions in solids: a view from a historical perspective

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Historical analysis suggests that the basic kinetic concepts of reactions in solids were inherited from homogeneous kinetics. These concepts rest upon the assumption of a single-step reaction that disagrees with the multiple-step nature of solid-state processes. The inadequate concepts inspire such unjustified anticipations of kinetic analysis as evaluating constant activation energy and/or deriving a single-step reaction mechanism for the overall process. A more adequate concept is that of the effective activation energy, which may vary with temperature and extent of conversion. The adequacy of this concept is illustrated by literature data as well as by experimental data on the thermal dehydration of calcium oxalate monohydrate and thermal decomposition of calcium carbonate, ammonium nitrate and 1,3,5,7-tetranitro-1,3,5,7-tetrazocine.

...we must focus our main attention on avoiding all inconsistencies and logical mistakes and on not smuggling in tacit concepts or assumptions, and ensure on the contrary that we become most clearly aware of all hypotheses we rely on.

Ludwig Boltzmann

1. Introduction

The epistemological value of concepts cannot be overestimated. They determine the soundness of experimental results and guide their interpretation. In fact, we see physical phenomena through the eyeglasses of concepts. The down side of this is that we see only as much as the concepts allow us to see. Because the concepts generalize a certain class of physical phenomena, the trustworthiness of the phenomenological picture seen is determined by the adequacy of the concept for a phenomenon under study. If the phenomenon does not entirely fall into the class of the phenomena represented by the concept, the use of the latter is most likely to result in a deformed phenomenological picture.

The basic kinetic concepts such as ‘reaction rate’, ‘rate constant’, ‘activation energy’ and ‘reaction order’ had formed by the end of the nineteenth century. When studying the kinetics of the inversion of cane sugar in the presence of acids, Wilhelmy [1] discovered that the rate of the process is proportional to the amount of remaining cane sugar as follows:

$$-\frac{dx}{dt} = k(C - x), \quad (1)$$

where t is the time, C is the initial amount of cane sugar, x is the inverted amount and k is the rate constant (Wilhelmy called it the ‘conversion constant’). Guldberg and Waage [2] developed a general rate equation that they called the ‘law of mass action’.

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van't Hoff [3] showed that for n reactants taken in equivalent amounts the law of mass action may be written as

$$-\frac{dC}{dt} = kC^n, \quad (2)$$

where C is the concentration of each of the reactants and n is the number of molecules involved in the reaction or the reaction order. Arrhenius [4] introduced the concept of heat (or energy) of activation to describe the temperature dependence of the reaction rate.

All the above-mentioned kinetic concepts were generalizations of empirical knowledge about homogeneous reactions. Hence, we should not generally expect an accurate phenomenological description to result from the application of these concepts to reactions of solids. Nevertheless these concepts have been extensively used in solid-state kinetics since the early twentieth century [5].

This work reviews the history of introducing homogeneous kinetics concepts into the kinetics of solid-state reactions. The inadequacy of these concepts is emphasized and the development of alternative concepts is considered. It should be stressed that the present discussion primarily applied to the kinetics studies that are based on measuring the overall (i.e. not species-specific) physical properties such as the mass loss, heat release, volume and pressure. These techniques cover the overwhelming majority of kinetic studies of thermally stimulated reactions such as decomposition, oxidation, reduction and crystallization of solids. More details on these techniques and their applications can be found in the classical text by Wendlandt [6].

2. Concept of single-step reaction

According to equation (2), the state of a reacting system can be adequately described by the concentration of a single reactant, even though several reactants take part in the reaction. Equation (2) was obtained by assuming that the consumption rates of all reactants are equal. This holds only if all n molecules react at once, that is in a single step. Furthermore, equation (2) parametrizes the reaction rate as a function of temperature (via the Arrhenius equation) and concentration and these are independent. This means that the temperature does not affect the ratio of the individual consumption rates. Again, this holds only for a single-step reaction. This limitation of equation (2) was mentioned by Ostwald [7], who warned that 'from this there is only a deviation when several independent reactions take place simultaneously, and such cases have not yet been investigated with respect to their velocity of reaction'. The rates of multiple-step reactions were experimentally studied on the verge of the twentieth century [8–11]. However, the general concept of multiple-step kinetics formed much later [12].

The concept of the single-step reaction was introduced into solid-state kinetics by Lewis [5] in his pioneering work on the kinetics of the autocatalytic thermal decomposition of silver oxide that was described as follows:

$$\frac{d\alpha}{dt} = k\alpha(1 - \alpha). \quad (3)$$

Therefore the concept was borrowed from homogeneous kinetics and applied to a heterogeneous reaction of a solid. Because the concentration could not be used to

Table 1. Set of reaction models applied to describe thermal decomposition in solids.

Reaction model	$f(\alpha)$	$g(\alpha)$
1 Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
2 Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
3 Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
4 Power law	$\frac{2}{3}\alpha^{-1/2}$	$\alpha^{3/2}$
5 One-dimensional diffusion	$\frac{1}{2}\alpha^{-1}$	α^2
6 Mampel (first order)	$1 - \alpha$	$-\ln(1 - \alpha)$
7 Avrami-Erofeev	$4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$	$[- \ln(1 - \alpha)]^{1/4}$
8 Avrami-Erofeev	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	$[- \ln(1 - \alpha)]^{1/3}$
9 Avrami-Erofeev	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	$[- \ln(1 - \alpha)]^{1/2}$
10 Three-dimensional diffusion	$2(1 - \alpha)^{2/3}[1 - (1 - \alpha)^{1/3}]^{-1}$	$[1 - (1 - \alpha)^{1/3}]^2$
11 Contracting sphere	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
12 Contracting cylinder	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$

characterize the state of a reacting solid, it was replaced [5] with the extent of conversion, α . This value is determined as a relative change in the measured overall properties. The extent of conversion is also an overall (i.e. not species-specific) characteristic that generally cannot be broken down to the contributions of single reaction steps. For this reason, α cannot uniquely represent the state of a solid that engaged in a multistep reaction.

Since the middle 1920s the multiple-step nature of solid-state reactions became more and more obvious. In their study of the thermal decomposition of silver oxalate, MacDonald and Hinshelwood [13] suggested for the first time that the decomposition involves two different rate processes, which are the formation of silver nuclei and their subsequent growth. Bruzs [14] showed that the kinetics of the thermal decomposition of cobalt carbonate cannot be described as a single-step process; a mechanism of two consecutive reactions was proposed as an alternative. For the thermal decomposition of mercury fulminate, Garner and Hailes [15] suggested that nucleation is accompanied by the process of nuclei branching, which is characterized by its own rate constant.

Furthermore, the individual processes of nucleation and nuclei growth also occur as multiple steps. The multiple-step nucleation mechanisms were first proposed by Bagdassarian [16] and Erofeev [17]. Later these mechanisms were generalized by Allnatt and Jacobs [18], whose model accounts for different rate constants of successive nucleation steps. The process of nuclei growth also does not have to obey single-step kinetics because its rate may differ along different crystallographic axes [19]. Additionally, most solid-state reactions are studied on polycrystalline samples, in which the reaction rates are different for crystals of different sizes.

Hence, solid-state reactions tend to occur in multiple steps that have different rates. This obviously casts doubts upon the general adequacy of the concept of single-step reaction to the kinetics in solids.

3. Concept of the reaction model as representative of the mechanism

van't Hoff [3] proposed to employ kinetic analysis for mechanistic interpretations. According to his idea, the experimentally determined reaction order equals the number of molecules participating in a reaction step. For instance, for the reaction of bromine with fumaric acid, van't Hoff has found the reaction order to be 1.87, from which he concluded that the reaction is bimolecular [3]. van't Hoff's idea was

extensively exercised in homogeneous kinetics and formed the concept of reaction order as a representative of the mechanism [12]. Nevertheless, Hinshelwood [20] showed that for the heterogeneous gas-phase reactions the kinetically determined order is not necessarily equal to the number of molecules participating in the reaction step.

In solid-state kinetics, the concept of reaction model, as a representative of the mechanism, started to form in the 1920s, when MacDonald and Hinshelwood [13] introduced the idea of the formation and growth of product nuclei in a decomposing solid. This idea spurred intensive development of mechanistic models. Jacobs and Tompkins [21] gave the first representative account of these mechanisms and corresponding equations. The most recent compendium of the reaction models is given by Galwey and Brown [22]. Table 1 collects together some of these models.

The mechanistic interpretations of solid-state kinetics are based on the concept of single-step reaction as given by

$$\frac{d\alpha}{dt} = kf(\alpha), \quad (4)$$

where $f(\alpha)$ is the reaction model that represents a certain solid-state mechanism. The concept of the reaction model suggests that solid-state mechanisms give rise to the characteristic α versus t or $d\alpha/dt$ versus t plots or mathematical functions (i.e. $f(\alpha)$). Then one can compare experimental data against a set of the model plots and choose the model that accurately reproduces data. This enables the data to be interpreted in terms of the mechanism represented by the chosen reaction model. To choose the model, one can use the reduced time plots [22] of α against t/t_α where t_α is the time to reach a certain value of α (usually 0.5 to 0.9). According to the integral form of equation (4), that is

$$g(\alpha) \equiv \int_0^\alpha \frac{d\alpha}{f(\alpha)} = kt, \quad (5)$$

the reduced time plots are independent of the temperature, if the concept of a single-step reaction holds.

Let us try to choose the reaction model based on thermogravimetric data for the thermal decomposition of CaCO_3 (calcite) and NH_4NO_3 . For each of these processes the reduced time plots corresponding to different temperatures happened to be almost undistinguishable and were replaced with averaged plots (figure 1). As we can see, the experimental data do not closely follow any of the model plots that is not an atypical situation. In such a case, the commonplace practice is to choose the model that gives the best statistical fit of experimental data. Then the mechanistic interpretations are made in terms of the best-fitting model. This practice suffers from such inherent flaws as the unavoidably incomplete list of the models involved in kinetic analysis, irrelevance of statistical choice to physical meaning of the models, and ambiguous correlation between the mechanism and the model that represents it [23]. Because of these flaws, it cannot practically lead to unambiguous mechanistic interpretations, even in the case of close agreement between experimental data and a reaction model. Therefore, even if we disregard the above-mentioned inconsistencies of the concept of single-step reaction, the concept of the reaction model appears to be ineffective in learning the mechanism of solid-state reactions.

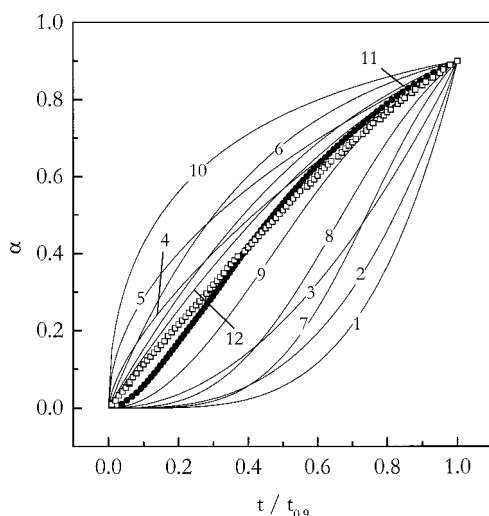


Figure 1. Reduced time plots for the reaction models (—) (as enumerated in table 1) and isothermal experimental data for the thermal decomposition of NH_4NO_3 under ambient pressure of N_2 (\square) and CaCO_3 under a vacuum of 0.5 mbar (\bullet). The decomposition data were averaged over three temperatures (156, 160 and 168°C) for NH_4NO_3 and over six temperatures (515, 520, 530, 535, 540 and 550°C) for CaCO_3 .

4. Concept of constant activation energy

Arrhenius [4] empirically established that the temperature dependence of the rate constant can be described as follows:

$$\frac{d(\log k)}{dT} = \frac{B}{T^2}. \quad (6)$$

In equation (6), B is $1/R$ times the heat absorbed in the process of transformation of inactive molecules into active molecules or, in other words, the heat of activation [4]. Usually equation (6) is written in the integral form as follows:

$$k = A \exp\left(-\frac{E}{RT}\right), \quad (7)$$

where E is the activation energy (the heat of activation), A is the pre-exponential factor, T is the temperature and R is the gas constant.

This equation represents Arrhenius' [4] hypothesis that the normal (i.e. inactive) molecules are in an endothermic equilibrium with the active molecules, which take part in the reaction. According to Arrhenius, the value E in equation (7) is the heat absorbed in the process of transformation of inactive molecules into active molecules or, in other words, the heat (or energy) of activation. Because of its original thermodynamic meaning, E was expected to be a constant, which is independent of a pathway taken by a system from an initial to a final state. However, the activation energy seems to have been 'misbehaving' since the time of the earliest kinetic measurements. An intriguing example can be found in van't Hoff's *Etudes de Dynamique Chimique* [3]. In this book, van't Hoff gives a table for the temperature dependence of the rate constants, which were determined by Schwab for the reaction between sodium chloracetate and sodium hydroxide:



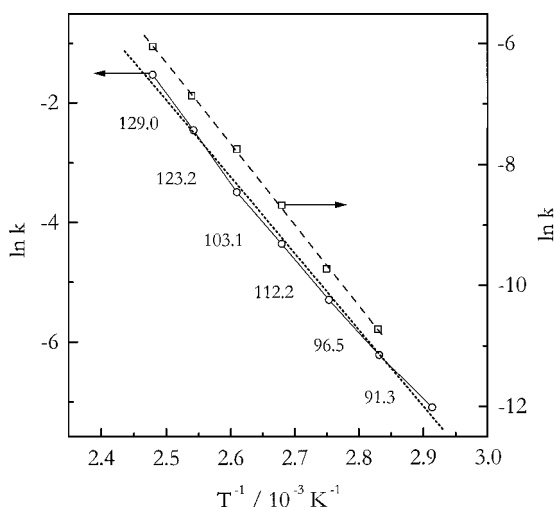


Figure 2. Arrhenius plots for the reaction between sodium chloracetate and sodium hydroxide (○) and for hydrolysis of monochloroacetic acid (□). The numbers by the linear segments represent the respective values of the activation energy in kilojoules per mole. The straight broken and dotted lines represent the least-squares fits for respective data sets.

The titrometrically measured concentration of NaOH was found to follow the equation of a bimolecular reaction [3]:

$$\frac{1}{C} = kt + \text{constant}. \quad (9)$$

As seen from figure 2 the obtained rate constants give rise to a nonlinear Arrhenius plot. Although the whole set of data can be fit by an Arrhenius line that yields $E = 106.8 \pm 7.4 \text{ kJ mol}^{-1}$, some values of E obtained from the Arrhenius lines connecting two neighbouring points lie outside the above confidence limits. Obviously, it is difficult to make indisputable conclusions based on data that were obtained more than a century ago and for which neither random nor systematic errors were reported. However, the data appear to be statistically sound because each rate constant was estimated as an average of three to six experiments [3]. We cannot completely rule out the chance that the reported rate constants might be subject to a systematic error, which varies with the temperature and might, therefore, introduce some nonlinearity into the Arrhenius plot. Nevertheless a perfectly linear Arrhenius plot is obtained for the rate constants determined by Schwab (see [3]) for a bimolecular reaction of hydrolysis of monochloroacetic acid:



Now, if the above-mentioned nonlinearity was exclusively caused by the temperature variation of the systematic error, then we would have observed a similar effect for hydrolysis of monochloroacetic acid that was studied over almost the same temperature region. Consequently, the nonlinear Arrhenius plot in figure 2 appears to present one of the earliest examples of the temperature dependence of the activation energy. The authenticity of nonlinear Arrhenius plots was first recognized by Hinshelwood [20], who pointed out that such a plot 'is almost certain indication that the observed reaction is a composite one made up of two or more concurrent reactions differently influenced by temperature'.

In solid-state kinetics, equation (7) was first applied by Bruzs [14], who estimated the activation energies of the thermal decomposition of carbonates of cobalt and zinc. Later, the application of the Arrhenius equation to solid-state reactions finds its theoretical justification in the studies of Polanyi and Wigner [24], Bradley [25, 26], Topley [27], Shannon [28], Cordes [29] and, most recently, Galwey and Brown [30]. Because all these theoretical treatments are based on the concepts of a single-step reaction, they naturally give rise to the concept of constant activation energy that holds for an elementary step of a solid-state reaction. However, the regular experimental techniques are not species specific and, therefore, are not capable of measuring the kinetics of elementary steps. These techniques produce overall kinetic data that represent a tangled interplay of different single species-dependent steps. These may include not only the earlier mentioned multiple chemical steps, but also such processes as sublimation, adsorption-desorption of gaseous products or reactants on the surface of a reacting solid and diffusion of gaseous products or reactants through a solid product or reactant. These steps have their own activation energies, which are likely to be different. When we evaluate the activation energy from the overall kinetic data, we unavoidably obtain an effective activation energy that is a composite value determined by the activation energies of the individual steps and by their relative contributions to the overall reaction rate. For this reason, the effective activation energy is generally a function of either temperature or both temperature and extent of conversion.

For instance, Fischbeck [31] stressed that the rates of both diffusion and reaction should be taken into account when describing the kinetics of reactions of solids. He defined the reaction rate of a process as a ratio of the 'driving force' to the 'reaction resistance'. In the general case, the rate of a solid-state process is determined [31] by the total resistance which is the sum of the reaction resistance W_R and diffusion resistance and W_D :

$$W = W_R + W_D. \quad (11)$$

Because the resistance is analogous to the reciprocal rate constant [31], equation (11) can be rewritten as follows:

$$\frac{1}{k_{\text{ef}}} = \frac{1}{k_R} + \frac{1}{k_D}, \quad (12)$$

where k_{ef} is the effective (total) rate constant, and k_R and k_D are the rate constants for reaction and diffusion respectively. From equation (12), one can easily deduce the effective activation energy for a process that involves both chemical reaction and diffusion:

$$E_{\text{ef}} = -R \left(\frac{d(\ln k_{\text{ef}})}{dT^{-1}} \right) = \frac{E_D k_R + E_R k_D}{k_R + k_D}. \quad (13)$$

Because both k_R and k_D vary with temperature, the effective activation energy in equation (13) is also temperature dependent. This effect has been experimentally observed by Fischbeck *et al.* [32] in the form of nonlinear Arrhenius dependences. Later Zeldowitsch [33] theoretically predicted a decrease in the activation energy with increasing temperature for heterogeneous reactions of powders and porous solids that occur in a 'mixed' diffusion-kinetic regime.

Even if a solid-state process is controlled by diffusion alone ($k_D \ll k_R$), we still may observe a variation in the activation energy of diffusion with temperature. Jost [34] demonstrated that a minor variation in the activation energy may be caused by

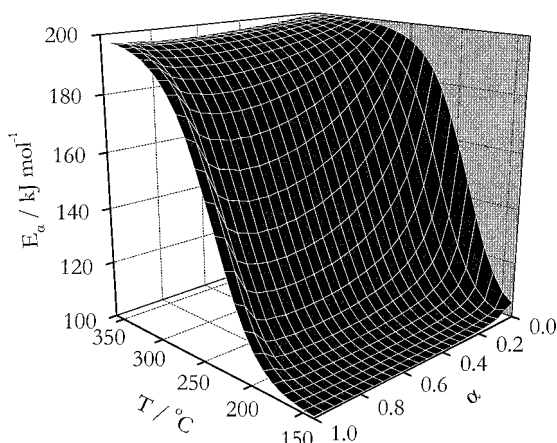
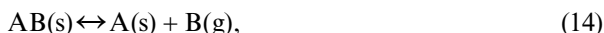


Figure 3. Surface plot of activation energy as a function of extent of conversion and temperature for the simulated process (equation (16)).

thermal expansion. On the other hand, Mapother *et al.* [35] experimentally found that a change in the diffusion mechanism may cause a very significant (more than two times) variation in the activation energy of diffusion. Not only diffusion but an apparently simple process of sublimation tends to demonstrate multiple-step kinetics [36, 37].

Many solid-state decompositions are reversible. For the reversible process



Pavlyuchenko and Prodan [38, 39] have shown that the effective activation energy is given by the following equation:

$$E_{\text{ef}} = E_2 - \lambda + mQ \frac{P_0^m}{P_0^m - P^m} \quad (15)$$

where E_2 is the activation energy of the reverse reaction, λ is the heat of adsorption, m is a constant ($0 < m \leq 1$), Q is the thermal effect of reaction, P_0 is the equilibrium pressure, and P is the partial pressure of the gaseous product B. Equation (15) suggests that, if P is not negligible compared with P_0 , then the effective activation energy should vary with the temperature, because the equilibrium pressure is a function of temperature. This may explain the experimental finding by Centnerszwer and Bruzs [40] that the temperature coefficient for the thermal decomposition of cadmium carbonate decreases systematically with increasing temperature (from 2.76 to 1.69 at T from 376 to 400°C). The temperature coefficient was estimated as an increase in the rate constant produced by 10°C increase in temperature [40].

The dependence of the effective activation energy on both temperature and extent of conversion can be exemplified by a decomposition process that occurs via two parallel pathways as follows:



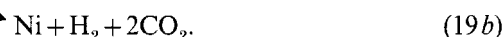
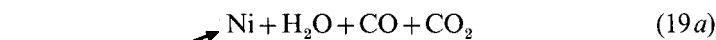
Parallel reactions have been reported for the thermal decomposition of nickel formate [41, 42], dolomite [43], cobalt(III) ammine azides [44–46], and magnesium and zinc oxalates [47]. If the pathways follow different reaction models, the overall decomposition rate is given by

$$\frac{d\alpha}{dt} = k_1 f_1(\alpha) + k_2 f_2(\alpha). \quad (17)$$

By taking the logarithmic derivative of the reaction rate at a constant extent of conversion, we can determine the effective activation energy at each α as follows:

$$E_\alpha = -R \left(\frac{d[\ln(d\alpha/dt)]}{dT^{-1}} \right)_\alpha = \frac{E_1 k_1 f_1(\alpha) + E_2 k_2 f_2(\alpha)}{k_1 f_1(\alpha) + k_2 f_2(\alpha)}, \quad (18)$$

where the subscript α denotes values related to a constant extent of conversion. For instance nickel formate was found [41] to decompose as follows:



For the temperature region 215–250 °C, Balandin *et al.* [41] determined that the later stage of decomposition prevalently occurs via channel (19b), for which $f(\alpha) = (1 - \alpha)^{2/3}$ and $E = 200 \text{ kJ mol}^{-1}$. According to Bircumshaw and Edwards [42] the two channels are not resolved in time at lower temperatures (165–180 °C). The Prout–Tompkins equation $f(\alpha) = \alpha(1 - \alpha)$ was found [42] to describe the whole process, the initial (acceleratory) stage of which has an activation energy of 99.5 kJ mol^{-1} . Although the latter activation energy and reaction model cannot be directly assigned to the individual channel (19a), it is reasonable to conclude that the channels (19a) and (19b) have different activation energies and follow different reaction models. Let us now consider for illustration purposes a similar process that involves two parallel reactions having the following kinetic triplets: $f_1(\alpha) = (1 - \alpha)^{2/3}$, $E_1 = 200 \text{ kJ mol}^{-1}$, $A_1 = 10^{16} \text{ min}^{-1}$, and $f_2(\alpha) = \alpha(1 - \alpha)$, $E_2 = 100 \text{ kJ mol}^{-1}$, $A_2 = 10^7 \text{ min}^{-1}$. Substitution of these triplets in equation (18) gives rise to the effective activation energy, which is obviously a function of both temperature and extent of conversion (figure 3).

Therefore, the concept of constant activation energy should not guide experimental determination of the activation energies, whose values are effective by the nature of measurements and may, thus, be variable. The concept of variable activation energy is more adequate to the multiple-step nature of solid-state reactions. It should be used to describe the temperature dependence of the overall reaction rates.

5. The concepts and two alternative approaches to kinetic analysis

Since the very first kinetic studies, the prevalent approach to kinetic evaluations has been force fitting of experimental data obtained at a single temperature or at a single heating rate to various single-step reaction models. The usual outcome of this procedure is determination of a single reaction model and a constant value of the activation energy for the overall process. Needless to say, this approach directly materializes the concept of single-step reaction, the concept of reaction model as a

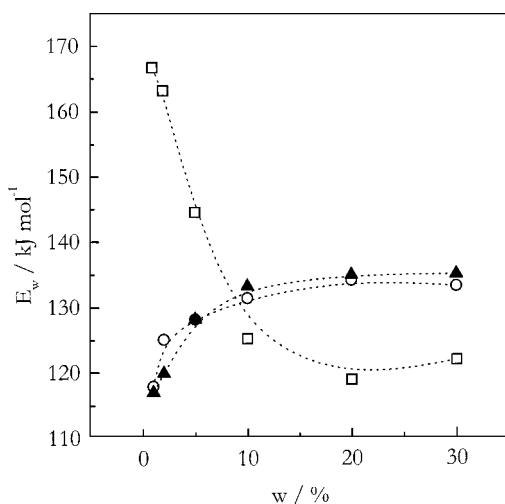


Figure 4. Activation energy E_w as a function of the mass loss w for the decompositions of silk (□), manila paper (○) and filter paper (▲). The mass loss is given as a percentage of the initial mass.

representative of the mechanism, and the concept of constant activation energy. For this reason, this approach inevitably produces kinetic parameters that inherit all the above-mentioned inconsistencies of these concepts.

The concept of variable activation energy is represented by the model-free isoconversional methods. These methods use the rate data related to a constant conversion which allows one to eliminate the dependence of the reaction rate on conversion and, therefore, on the reaction model. For a single-step reaction, rearrangement of equation (3) for a constant extent of conversion gives

$$\left(\frac{d[\ln(d\alpha/dt)]}{dT^{-1}} \right)_\alpha \equiv \left(\frac{d(\ln k)}{dT^{-1}} \right)_\alpha + \left(\frac{df(\alpha)}{dT^{-1}} \right)_\alpha = -\frac{E_\alpha}{R}. \quad (20)$$

Because the second term of the sum in equation (20) is zero, the effective activation energy of a single-step reaction is independent of the extent of conversion. As was mentioned earlier, the overall extent of conversion does not uniquely determine the composition of the solid involved in multiple-step reactions. As a result, the isoconversional methods usually yield E_α values that vary with α and T (cf. figure 3). This dependence reflects the variation in relative contributions of single steps to the overall reaction rate and can, therefore, be used to detect multiple-step kinetics. Additionally, exploring the E_α dependences may be very helpful in drawing mechanistic conclusions [48], which is not yet the reaction mechanism, but a path to it that should further be followed only by using species-specific experimental techniques.

The first application of the isoconversional methods dates back to 1925, when Kujirai and Akahira [49] applied such a method to the data on the thermal decomposition of insulating materials under isothermal conditions. We used their method and data to evaluate the activation energy as a function of mass loss w . The found values of the activation energy demonstrate a noticeable variation with w (figure 4). For non-isothermal conditions, isoconversional methods were developed in the

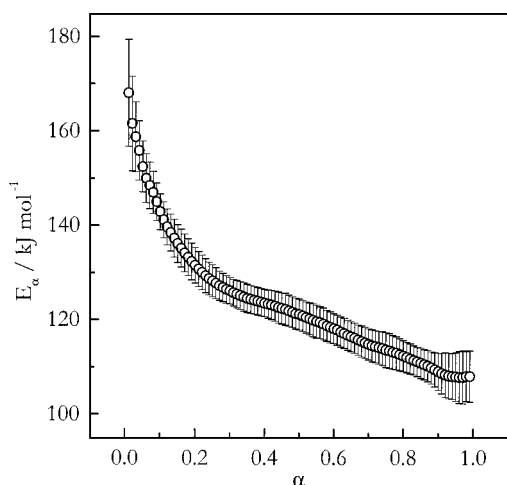


Figure 5. Dependence of the activation energy on extent of CaCO_3 conversion determined using the isoconversional method. The thermal decomposition of CaCO_3 was studied by thermogravimetric method under vacuum (0.5 mbar) at heating rates of $1.8\text{--}10^\circ\text{C min}^{-1}$.

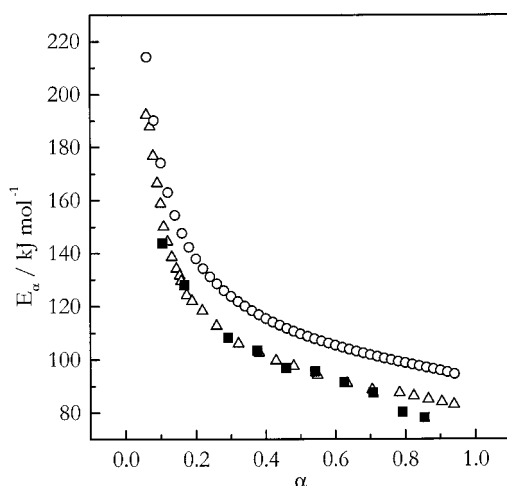


Figure 6. Dependence of the activation energy on extent of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ dehydration determined by using isoconversional methods: (■), data from [57]; (Δ), data from [58]; (\circ), present data.

1960s by Friedman [50], Ozawa [51] and Flynn and Wall [52]. Friedman [50] and Ozawa [51] found the activation energy to vary with extent of decomposition of a phenolic plastic and of Nylon 6 respectively. Friedman also demonstrated that the observed variation markedly exceeded confidence intervals for the activation energy [50]. Using simulated multiple-step kinetics, Flynn and Wall [52] explained the phenomenon of variable activation energy and therefore ‘legalized’ its existence.

It seems to be unfortunate that the above variations in the activation energy have been observed for quite complex systems, whose decompositions naturally demonstrate multiple-step kinetics. Therefore the importance of this phenomenon was not immediately obvious. However, the further application of the isoconversional methods

Table 2. Arrhenius parameters for the thermal decomposition of HMX at 0.2°C min⁻¹.

Model	<i>g</i> (α)	<i>E</i> (kJ mol ⁻¹)	log[<i>A</i> (min ⁻¹)]	– <i>r</i>
1	$\alpha^{1/4}$	21.3	– 0.6	0.9327
2	$\alpha^{1/3}$	31.0	0.5	0.9424
3	$\alpha^{1/2}$	50.4	2.7	0.9501
4 ^a	$\alpha^{3/2}$	167.0	14.8	0.9582
5 ^a	α^2	225.3	20.7	0.9591
6	– ln(1 – α)	125.9	10.8	0.9444
7	[– ln(1 – α)] ^{1/4}	25.6	0.0	0.9205
8	[– ln(1 – α)] ^{1/3}	36.7	1.3	0.9299
9	[– ln(1 – α)] ^{1/2}	59.0	3.7	0.9378
10	[1 – (1 – α) ^{1/3}] ²	246.1	22.2	0.9536
11	1 – (1 – α) ^{1/3}	119.1	9.5	0.9508
12	1 – (1 – α) ^{1/2}	116.2	9.4	0.9530

^a ‘Best fit’.

to numerous processes has suggested [23, 48] that the significant variations (i.e. variations that exceed confidence limits) in the activation energy are quite typical of thermally stimulated reactions in ionic salts as well as in polymers. Vyazovkin and Wight have recently reported the significant *E_α* dependences and their mechanistic interpretations for the thermal decompositions of ammonium dinitramide [53] and ammonium perchlorate [54]. Significant variations in *E_α* are observed for even simpler reactions such as the thermal decomposition of CaCO₃ (figure 5), and the thermal dehydration of monohydrates of Li₂SO₄ [55, 56] and CaC₂O₄ [57, 58]. Ninan and Nair [59] have extensively applied fitting of various single-step reaction models to thermogravimetric data on dehydration of CaC₂O₄·H₂O under non-isothermal conditions. All the reaction models were found [59] to give excellent data fits. However, a variation in the reaction models resulted in significantly different activation energies, whose extreme values showed an approximately fivefold difference [59]. This casts serious doubts upon the ability of the single-step model-fitting method to produce consistent kinetic results. On the other hand, we applied an advanced isoconversional method [60] to mass loss data on dehydration of CaC₂O₄·H₂O at the heating rates 1–10°C min⁻¹ and found the resulting *E_α* dependence to be in excellent agreement with the earlier reported dependences (figure 6).

The above-mentioned uncertainty in the Arrhenius parameters obtained by model fitting makes them virtually useless for practical purposes such as predicting the reaction kinetics at an arbitrary temperature. Rearrangement of equation (5) to give

$$t_{\alpha} = \frac{g(\alpha)}{A \exp(-E/RT_0)} \tag{21}$$

allows evaluation of the time *t_α* to reach the extent of conversion α at an arbitrary temperature *T₀*. The use of this approach can be illustrated for the thermal decomposition of 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). We used the Coats–Redfern [61] method to estimate the *E* and *A* values from mass loss data obtained at the heating rates 0.2–0.9°C min⁻¹. Statistical analysis of the correlation coefficients (*r* in table 2) suggests that models 4 and 5 represent the two best fits, which are equivalent from the statistical standpoint. As seen in figure 7, substitution of the respective parameters into equation (21) results in rather unsatisfactory predictions.

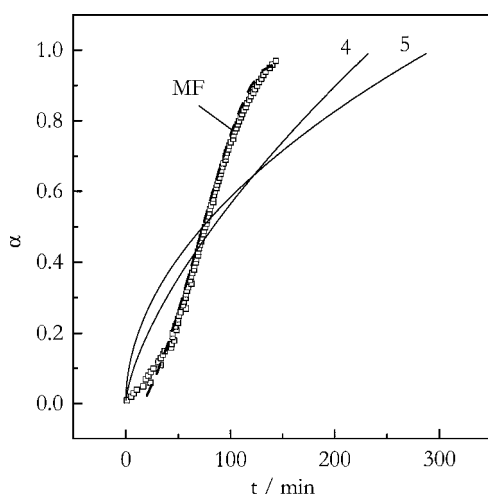


Figure 7. Predictions of the isothermal decomposition kinetics of HMX at 235°C. The solid curves 4 and 5 are calculated using equation (21) and the corresponding kinetic triplets in table 2. The broken curve labelled MF is the model-free prediction calculated using equation (22). The open squares indicate the experimental data.

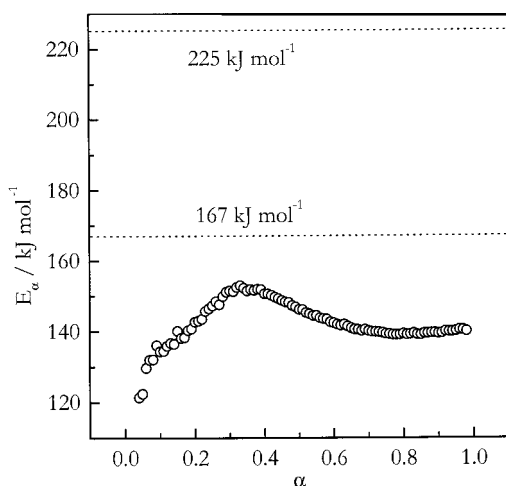


Figure 8. Dependences of the activation energy on extent of HMX conversion determined by the isoconversional method (○): (---), values corresponding to the best fits (models 4 and 5 in table 2).

Alternatively, the isoconversional method provides a model-free way of making kinetic predictions. The latter can be performed by substituting the E_α dependence into the following equation [48]:

$$t_\alpha = \frac{\int_0^{T_\alpha} \exp(-E_\alpha/RT) dT}{\beta \exp(-E_\alpha/RT_0)}, \quad (22)$$

where T_α is the temperature at which a given conversion is reached at an experimental heating rate β . The application of the advanced isoconversional method [60] to the HMX decomposition data yields the E_α dependence shown in figure 8. As we can see,

the activation energies corresponding to the best fits (table 2) are markedly greater than the activation energies estimated by the isoconversional method. Substitution of the obtained E_a dependence into equation (22) results in a prediction that is in excellent agreement with the actual isothermal measurements. The model-free approach to kinetic predictions opens up an opportunity for estimating the relative reactivity of solids by comparing the respective predicted times to reach the same extent of conversion at the same temperature.

Therefore, the isoconversional method lays a foundation for completely model-free kinetic analysis of thermally stimulated reactions of solids [48]. Based on the concept of a variable activation energy, this type of analysis appears to be more adequate for the actual complexity of solid-state reactions than the analysis based on the standard model-fitting approach.

6. Conclusions

Our brief historical review shows that solid-state kinetics inherited their basic concepts from the kinetics of much simpler reactions in homogeneous media. The central concept of a single-step reaction as well as the two derivative concepts (the concept of constant activation energy and the concept of reaction model as a representative of the mechanism) is inconsistent with the multiple-step nature of solid-state reactions. Although these concepts are contradictory to numerous experimental facts, which were discovered 40–50 years ago, they are prevalently used in current kinetic analyses. This is especially surprising in the light of more recent knowledge, which clearly demonstrates that solid-state reactions are much more involved than they appeared half a century ago. It is now recognized [22] that real solid-state reactions are often too complex to be described in terms of a single pair of Arrhenius parameters and the traditional set of reaction models. Experimental evidence suggests that the solid-state reactions are not necessarily localized on the interface boundaries and that the new product phase may form in the modified material, in the unchanged reactant beneath or in the transition zone [22]. The understanding of the macrokinetic nature of the reaction zone stimulates development of diffusion–kinetic models capable of explaining the formation of dissipative structures in reacting solids [62]. New concepts based on the ideas of chemical pressure [63] and distributed reactivity [64] have been proposed. Molecular dynamics simulations are efficiently used to treat diffusion [65] and surface processes [66] of solids. The mathematical apparatus of fractals is actively scrutinized in order to reach a more adequate description of reactions of solids [67, 68].

The accumulation of empirical knowledge and attempts to obtain its theoretical generalization should ultimately result in building an adequate conceptual basis for the kinetic analysis of solid-state reactions. In the meantime the acceptance of the concept of variable activation energy seems a reasonable compromise between the actual complexity of solid-state reactions and oversimplified methods of describing their kinetics.

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