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Kinetic effects of pressure on decomposition of solids

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ABSTRACT

The kinetics of thermal decomposition of solids is discussed in connection with three major approaches to inducing pressure: by manipulating pressure of the product gas, by changing pressure of an inert gas, and by applying a mechanical force. The first two approaches are implemented in differential scanning calorimetry (DSC) and thermogravimetry (TGA), whose upper pressure limit is in the MPa range. The third approach is implemented in diamond anvil cells that extend measurements to the GPa range. In the GPa range a response of the rate to pressure is determined by the sign of the activation volume change. In the MPa range this response is determined by pressure of the gaseous product in the reaction zone. Manipulating the product gas pressure affects directly the kinetics of reversible decompositions as described by a number of models. Changing pressure of an inert gas results in indirect manipulation of pressure of the gaseous products that can engage in reaction with the reactant or another product and thus affect the kinetics of autocatalytic and reversible decompositions. These and other effects are discussed with the emphasis on changes in the activation energy and preexponential factor as a function of pressure, temperature, and conversion.

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1. Introduction

Studying the kinetics of the thermal decomposition of solids is a fundamental research endeavour. It is of crucial relevance to designing numerous industrial processes as well as to understanding the thermal stability (shelf-life) of various solid materials. In recent years, an interest in the kinetics of thermal decomposition of solids has been growing steadily due to the development of novel energy storage technologies. These include reversible dehydrogenation of solid hydrides for hydrogen storage [1–3] as well as reversible decomposition of carbonates, hyroxides, hydrates, sulfates and other solids for thermochemical energy storage [4–7].

The kinetics of solid state reactions builds upon the concepts of homogenous kinetics adjusted to heterogeneous, gas–solid, systems [8]. There appears to be a common consensus [9] that when a solid decomposes with production of gases, the rate of its decomposition should generally be described as a function of three variables: conversion (α), temperature (T), and pressure (P). Then, the basic rate equation takes the following general form:

$$\frac{d\alpha}{dt} = k(T)f(\alpha)h(P) \tag{1}$$

where $k(T)$ is the rate constant, $f(\alpha)$ is the reaction model, and $h(P)$ is the pressure term. Each of the terms in the right hand side of Equation (1) describes the dependence of the rate, $d\alpha/dt$, on the respective variable. Notwithstanding the equal importance of all three terms, the monographic literature on the subject almost exclusively focuses on the effects of conversion and temperature. For example, the most comprehensive book [10] on the thermal decomposition of solids provides an extensive theoretical discussion of both temperature and conversion dependencies but does not examine a single equation for the pressure term. To some extent this situation is justified because since 1960s the thermal decomposition kinetics has been routinely studied by using commercial thermal analysis instrumentation, i.e. in an open system under a flow of an inert gas. Under such conditions all the product gases, which may be potentially reactive toward the solid product and/or reactant, are expected to be removed effectively. In this circumstance, the partial pressure of the product gas and, therefore, the pressure term can be neglected. It means that the h(P) term can be eliminated from Equation (1) giving rise to the rate equation used most commonly today in kinetic analysis of the decomposition reactions.

Employing Equation (1) without the pressure term may be adequate in many cases. Nevertheless, one should never become oblivious of the pressure effect when studying the kinetics of decomposition. It should be stressed specifically that carrying out the reactions of decomposition under a flow of an inert gas does not guarantee the absence of any pressure effects. The latter can still manifest themselves in reversible and sometimes even in irreversible decompositions. These and many other effects are discussed in the present review article.

The overall objective of this article is to create a reasonably comprehensive treatise on the effect of pressure on the thermal decomposition kinetics. This objective is accomplished by critically surveying the literature. The survey considers different ways of inducing pressure

and focuses on the effects of pressure on the rate and the kinetic parameters of decomposition. This article is expected to close an important gap existing in the broadly available monographic literature that typically treats the subjects of thermal decomposition and thermal analysis without paying the due attention to the kinetic effects of pressure. It is hoped that this article would provide stimulating reading for researchers striving to gain more comprehensive and balanced understanding of the thermal decomposition kinetics.

2. Pressure term equations

Decomposition of many solids is reversible and follows the following general equation:

$$A_s \underset{k_2}{\overset{k_1}{\rightleftarrows}} B_s + C_g \qquad (2)$$

where A_s is the solid reactant, B_s is the solid product, C_g is the gaseous product, and k_1 and k_2 are the Arrhenius rate constants for the forward and reverse reaction respectively. For a reversible reaction, ignoring the pressure term in Equation (1) can result in unexpected and drastic changes in the kinetic parameters if the partial pressure of the product gas is not negligible. Of course, such changes would be expected when decomposition is run deliberately in the atmosphere that contains the product gas. On the other hand, it is important to recognise that they may also happen when decomposition is carried out in a flowing inert gas. The latter represents the conditions typically encountered in thermogravimetric analysers (TGA) and differential scanning calorimeters (DSC), i.e. the instruments used most commonly for exploring the kinetics of thermal decomposition. As mentioned earlier, these conditions are expected to remove the product gas as effectively as in vacuum and, thus, render product gas pressure negligible. This is not always the case. For example, the reversible decomposition of titanium hydride has been reported [11] to be much slower in a flow of helium than in vacuum, which means that a flow of an inert gas may be insufficiently effective in removing the gaseous products.

In addition, one should remember that the solid product B is formed as a layer on top of the reactant A, so that the gas C formed at the interface between A and B has to take a tortuous path through the pores and cracks in B to reach the gas phase (Figure 1). The phenomena of adsorption and diffusion are likely to slow down the escape of the product gas that may lead to its accumulation inside the product B layer. The consequence of this situation is that the decomposition kinetics is not necessarily controlled by the negligible partial pressure of the gas C in the gas phase. Rather, it may be determined by appreciably larger partial pressure of C in the reaction zone, i.e. at the interface between A and B. This situation also means that the product gas would have increased chances to engage in reactions with the solid product and/or reactant. Consequently, decomposition can unexpectedly demonstrate kinetic parameters characteristic of the process performed under some non-negligible partial pressure of the product gas. By kinetic parameters we mean the Arrhenius activation energy, E, and the preexponential factor, A, determined from the basic rate equation:

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha) h(P) \qquad (3)$$
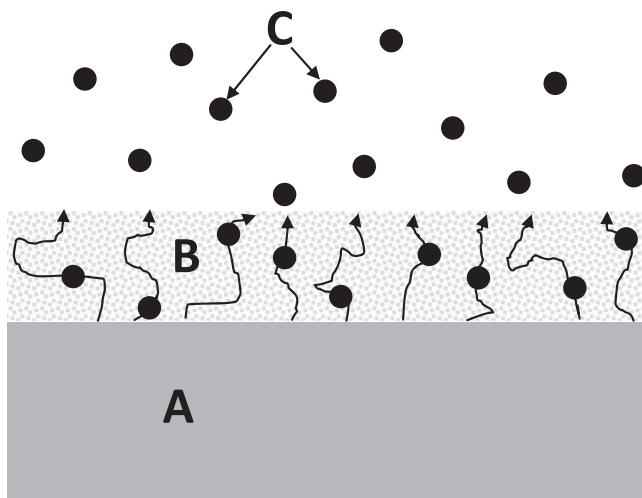
Figure 1. Schematic representation of reaction $A_s \rightleftarrows B_s + C_g$. Product gas molecules C formed via decompostion of solid reactant A may have to take a tortuous path through a layer of solid product B.

The effect of pressure on the rate of reversible decomposition is most commonly accounted for by introducing the following $h(P)$ term [9]:

$$h(P) = 1 - \frac{P}{P_0} \tag{4}$$

where P and P_0 respectively are the partial and equilibrium pressures of the gaseous product. In principle, to account for non-deal behaviour one should use the fugacity rather than pressure in Equation (4). However, reversible decompositions are normally studied at pressures well below the saturation value so that the fugacity coefficient [12] is negligibly different from unity. For example, reversible decomposition of hydrates usually occurs around 100°C. At this temperature, even at the saturation pressure ($\sim 10^5$ Pa) the fugacity coefficient is around 0.99 [13]. Taking into account that the dehydration kinetics are typically studied in the kPa range of pressures, the fugacity coefficient would be even closer to unity making the values of pressure and fugacity virtually identical.

The pressure term in the form of Equation (4) has been known at least since the Benton and Drake's work [14] on the reversible decomposition of silver oxide. They arrived at this type of the pressure dependence by assuming that the overall rate, r, of this process, is the difference of the rates of the forward and reverse reactions and that the rate of the latter is proportional to the partial pressure of the gaseous reaction product:

$$r = k_1 - k_2 P = k_1 \left(1 - \frac{P}{P_0}\right) \tag{5}$$

Although the intermediate steps of the derivation have not been presented in [14] they can be readily guessed by accounting for the fact that at equilibrium:

$$k_1 = k_2 P_0 \tag{6}$$

The substitution of k_2 from Equation (6) into Equation (5) yields the right hand side of Equation (5). Equation (5) holds for a reaction of the first-order with respect to the gaseous products. It is easy to demonstrate that for a n-th order reaction the pressure term takes the following form:

$$h(P) = 1 - \left(\frac{P}{P_0}\right)^n \tag{7}$$

This form of the pressure dependence is encountered much more rarely [15–17] in kinetic analyses than Equation (4).

It needs to be mentioned that the same type of the pressure dependence (Equation 5) has been obtained by other workers although in a different manner. Barret [18] has derived such pressure dependence for the reversible decomposition through the formation of an adsorbed intermediate. Searcy and Beruto [19] have arrived at a similar equation by assuming that diffusion of the gaseous product is a limiting step of a reversible decomposition. In this situation (Figure 1), diffusion of the product gas is treated [19,20] as the Knudsen flow. Reading et al. [21] have demonstrated that this relationship can be arrived at from the transition state theory where the forward and reverse reactions go through the formation of the activated intermediate.

An even simpler form of the pressure dependence, viz.:

$$h(P) = P_o - P \tag{8}$$

is encountered in various studies of reversible decomposition [22–25]. Sometimes it is introduced without any justification [24,25] i.e. as a self-obvious fact. Indeed, it is an empirical fact that the rate of reversible decomposition increases in proportion to the difference between the equilibrium and partial pressure of the gaseous product. Nevertheless, this proportion does not have to be linear. To some extent one may justify it by drawing an analogy with the Fick's first law of diffusion, whose rate is linearly proportional to the concentration gradient or to the pressure gradient for a gas. Actually, a more adequate justification has been given in the early work of Zawadzki and Bretsznajder [22,23]. In their study of calcium oxide carbonation:

$$CaO + CO_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} CaCO_3 \tag{9}$$

The authors present [22] the overall rate of this process as the difference between the rates of the forward and reverse reactions:

$$r = k_1 P - k_2 \tag{10}$$

so that at equilibrium:

$$k_1 P_0 = k_2 \tag{11}$$

Then substitution of Equation (11) into Equation (10) gives rise to:

$$r = k_1(P - P_0) \tag{12}$$

Subsequently, they argue [23] that for the reverse process of calcium carbonate decomposition the rate should be as follows:

$$r = k_1(P_0 - P) \tag{13}$$

Recall that in Equation (13) k_1 still is the rate constant of the forward reaction from Equation (9), i.e. the reaction of carbonation. That is, if one writes the decomposition reaction in the regular form (Equation 2), k_1 in Equation (13) would have to be replaced with k_2. However, it is normal practice to expresses the overall rate of the reversible decomposition by using the rate constant for the forward reaction, i.e. k_1 from Equation (2). Unfortunately, the derivations provided by Zawadzki and Bretsznajder cannot justify the application of the pressure term in the form of Equation (8) in combination with the rate constant for the forward reaction of the reversible decomposition. Interestingly enough, the application of the logical flow of the original work [22] by Zawadzki and Bretsznajder to the reversible decomposition (Equation 2) leads to Equation (5) derived later [14] by Benton and Drake.

Some publications [26,27] make use of the power function of the pressure difference:

$$h(P) = (P_o - P)^n \tag{14}$$

It should be noted that such form of $h(P)$ appears to be entirely empirical as it cannot be justified by either an analogy with the Fick's law or by the reasoning used by Zawadzki and Bretsznajder. The latter does allow the first order reaction model (Equation 12) to be expanded to n-th order. Then, the $h(P)$ term would be the difference between the equilibrium and partial pressure, each of which raised to the power n.

Several workers [28–30] have advocated the use of the following rate equation for describing the kinetics of reversible decomposition:

$$\frac{d\alpha}{dt} = k(T)f(\alpha)\left[1 - \exp\left(\frac{\Delta G}{RT}\right)\right] \tag{15}$$

where ΔG is the difference in the free energy of the products and reactant. This equation is introduced by analogy with the one derived by Bradley [31] to describe the kinetics of solid–solid transitions. The bracketed term represents the thermodynamic driving force of the process. Note that this term is also found [32,33] in the rate equations describing the kinetics of a new phase growth and had been known at least since the classical work of Volmer [34].

It has been stated [35,36], although without elaboration, that for simple reversible processes (Equation 2)

$$1 - \exp\left(\frac{\Delta G}{RT}\right) = 1 - \frac{P}{P_0} \tag{16}$$

Indeed, the bracketed term in Equation (15) can be used to derive a pressure dependence but not in the aforementioned form. For derivation, one needs to recognise first that the exponential term in Equation (16) is the reciprocal equilibrium constant, K. Per the law of mass action, K for the reaction 2 is equal to the equilibrium pressure of the gaseous product. Therefore, the following holds:

$$1 - \exp\left(\frac{\Delta G}{RT}\right) = 1 - \frac{1}{K} = 1 - \frac{1}{P_0} \tag{17}$$

The right hand side of Equation (17) is unmistakably different from that in Equation (16). Unfortunately, the resulting pressure term is physically meaningless because it suggests that the condition of equilibrium would always be accomplished at $P_0 = 1$. Needless to say

that depending on the units chosen for measuring pressure, $P_0 = 1$ would represent very different values (e.g. 1 Pa vs 1 bar). Even if one chooses the units of bar, as the accepted convention dictates, it would mean that equilibrium in reaction 2 is always reached at 1 bar, which does not make any sense. Apparently, the thermodynamic driving force term used in the kinetics of phase transitions is not directly applicable to the kinetics of reversible decompositions.

A reasonable pressure dependence [37–41]

$$h(P) = \ln \frac{P_0}{P} \tag{18}$$

can be obtained by introducing the thermodynamic driving force in a different form. For instance, analysing decomposition of lanthanum nickel hydride Reilly et al. [38] argue that the process is driven by the difference in the hydrogen concentration on the surface of the decomposing particle and in its core. The latter concentration is considered constant (equilibrium). Replacing the concentrations with the pressures they derive the ΔG term, whose value is proportional to the right hand side of Equation (18).

The obtained pressure dependence (Equation 18) is reasonable in the sense that it predicts a reasonable effect of pressure on the reaction rate. Namely, the rate is zero at equilibrium ($P = P_0$), positive when $P_0 > P$, and negative when $P_0 < P$. Nonetheless, a logical argument can be raised against the form of the obtained term. By its meaning it is dimensionless energy ($\Delta G/RT$), just as E/RT in the Arrhenius temperature dependence of the rate constant in Equation (1). Thus, it seems more logical for this term to be in the form of the exponential function of the dimensionless energy that would give it a meaning of the probability analogous to the exponential term in the Arrhenius equation. Of course, the exponential function of $\ln(P_0/P)$ would yield the dimensionless pressure as in Equation (4). And, the pressure being directly proportional to the frequency of collisions is just another way of expressing the probability.

To describe the effect of the hydrogen pressure on the reversible dehydrogenation of sodium alanate, Lozano et al. [40,41] have employed $h(P)$ in the form of Equation (18) as well as in the form of Equation (19):

$$h(P) = \frac{P_0 - P}{P_0} \tag{19}$$

which is obtained as the first term of the Taylor expansion for $\ln(P_0/P)$. They ultimately have ended up using Equation (19). Incidentally, this empirically introduced equation is identical to Equation (4) that, as shown above, is derived from some meaningful physical models.

Following the work of Lozano et al. [40,41], Catti et al. [42] have introduced an empirical function to describe the process of reversible dehydrogenation:

$$h(P) = \exp\left(a \frac{P - P_0}{P_0}\right) \tag{20}$$

where a is a fit parameter, which is negative. It can be readily shown that up to a constant multiplier Equation (20) is the same as Equation (21) proposed earlier by

Khinast et al. [43]:

$$h(P) = \exp\left(-a'\frac{P}{P_0}\right) \tag{21}$$

where a' is a fit parameter, which is positive. In both cases (Equations 20 and 21), the exponential form has been justified as the form giving good data fits. At any rate, neither of these two equations can be recommended for a meaningful description of the reversible kinetics. The exponential function is always positive so that the respective $h(P)$ term cannot turn to zero at $P = P_0$ or become negative at $P_0 < P$. It means that such form of the pressure term cannot predict either equilibrium ($h(P)$ and $d\alpha/dt$ are zero) or reversing of the reaction ($h(P)$ and $d\alpha/dt$ are negative).

Of course the models discussed above do not exhaust all possible ways for describing the pressure effect on the kinetics of reversible decompositions. We should mention specifically the existence of more complex models [18,19,44–46] that account for additional steps involved in decomposition such as adsorption, desorption, diffusion, etc. However, in some limit all these models can be reduced to Equation (4), which appears to be the most economical yet meaningful description of the pressure effect on the kinetics of reversible decompositions. It is not, thus, surprising that even nowadays Equation (4) is invoked most commonly for obtaining insights into the intricacies of reversible decompositions [20,47–56]. In addition, Equation (4) is known [20,40,41,49,50,55] to be capable of predicting the kinetic behaviour outside the range of experimental measurements.

3. Experimental Arrhenius parameters for reversible decompositions

3.1. Basics

As stated in the previous section, the most common pressure dependent form of the rate Equation (3) is as follows:

$$\frac{d\alpha}{dt} = A\exp\left(\frac{-E}{RT}\right)f(\alpha)\left(1 - \frac{P}{P_0}\right) \tag{22}$$

Equation (22) can be used conveniently to explain a variety of effects observed when measuring the rate of reversible decompositions and parameterising its temperature dependence by applying the Arrhenius equation. First, Equation (22) indicates that decomposition starts when P_0 rises above P. This condition is normally accomplished by increasing temperature that makes the equilibrium pressure rise in accord with the van't Hoff isochore:

$$\ln K = \ln P_0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{23}$$

where ΔS^0 and ΔH^0 are the standard entropy and enthalpy changes for reversible decomposition.

For decomposition of calcium carbonate the equilibrium pressure of carbon dioxide changes with temperature as follows [57,58]

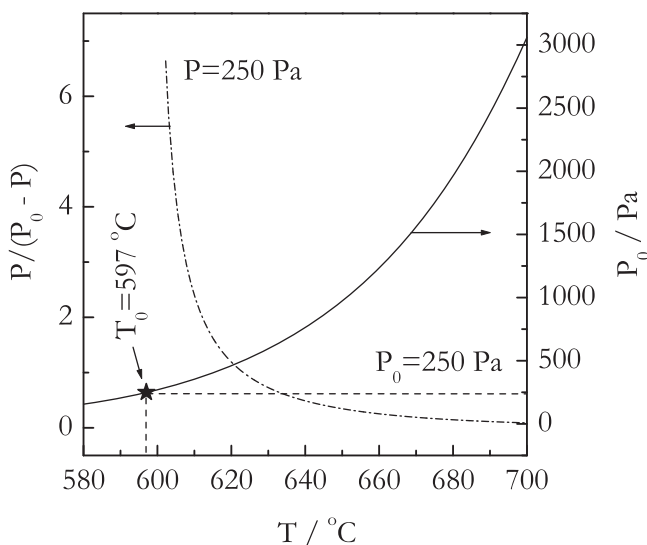$$\ln[P_0(\text{Pa})] = 29.18 - \frac{20590}{T} \tag{24}$$

Figure 2. Temperature dependence of the equilibrium pressure (solid line, right axis) and the pressure term from Equation (27) (dash-dot line, left axis) for thermal decomposition of calcium carbonate under 250 Pa of carbon dioxide. Star denotes the equilibrium temperature at which the equilibrium pressure becomes equal to the partial pressure.

Equation (24) can be used to estimate the equilibrium temperature, T_0. This is the temperature, at which the equilibrium pressure equals the partial pressure of the gaseous product. For example, if the pressure of carbon dioxide around solid calcium carbonate is set to be 250 Pa the decomposition should start on heating above $T_0 \approx 597°C$ (Figure 2). It is also clear from Figure 2 that increasing the partial pressure of the gaseous product would shift the reversible decomposition to higher temperature. Example of this effect for decomposition of calcium carbonate is given by Criado et al. [59].

Another important effect predicted by Equation (22) is the nonlinearity of the Arrhenius plots for reversible decompositions. As discussed by Lyakhov et al. [60], this nonlinearity should be observed when the runs are not conducted in vacuum, i.e. when $P > 0$. An impressive example of such effect has been provided by Bertrand et al. [61] for isothermal measurements on decomposition of magnesium chromate pentahydrate at two different pressures of water. The obtained Arrhenius plots have been of a concave down (i.e. negative second derivative) shape, and their curvature increased when temperature decreased toward T_0. To understand the origin of the respective nonlinear plots one must recognise the effective nature of the experimentally measured rate constant, k_{ef}. As such, it represents the product of the intrinsic rate constant and the pressure term:

$$k_{ef} = k(T) \left(1 - \frac{P}{P_0}\right) \tag{25}$$

In accord with Equation (25), k_{ef} depends on temperature not only via $k(T)$ but via P_0 as well (Equation 23). That is, it depends on temperature via a combination of two exponential terms. This is what makes the Arrhenius plot of $\ln k_{ef}$ vs. T^{-1} nonlinear.
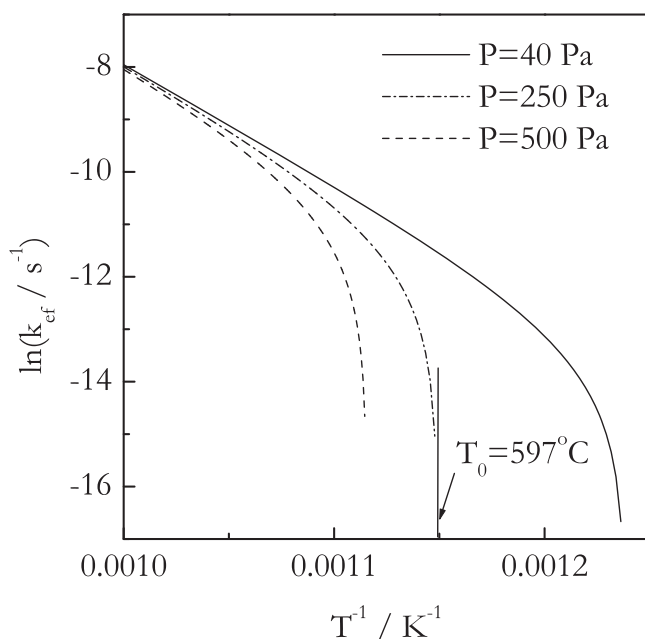
Figure 3. Arrhenius plots for the effective rate conctant simulated by Equation (25) for decomposition of calcium carbonate under different partial pressures of carbon dioxide. Arrow denotes the equilibrium temperature at 250 Pa.

To visualise the respective Arrhenius plot, we can use the Arrhenius parameters for decomposition of $CaCO_3$. For this process, the average values of the activation energy and preexponential factor are around $190 \, kJ \, mol^{-1}$ and $3 \cdot 10^6 \, s^{-1}$ [58]. Then plugging the temperature dependence of P_0 from Equation (24) in Equation (25) permits evaluation of k_{ef} at various temperatures and partial pressures of CO_2. Examples of the resulting Arrhenius plots are given in Figure 3. As in the work of Bertrand et al. [61] the plots are distinctly nonlinear (concave down) and their curvature increases quickly on approaching the equilibrium temperature T_0. It is worth mentioning that nonlinearity of Arrhenius plots in the vicinity of the equilibrium temperature is characteristic of a broad range of reversible processes. In particular, it is typical for the kinetics of the nucleation driven phase transitions (e.g. crystallization, melting, or solid–solid transformations) that occur not far from the equilibrium temperature [58,62].

Since the slope of the Arrhenius plot is directly proportional to the experimental value of the activation energy, one can conclude that this parameter should be temperature dependent, i.e. not constant. Discovering variable activation energy typically is a sign of a process that involves more than one step [63]. Obviously, any reversible reaction is a combination of the forward and reverse steps, i.e. more than one step. The relative contribution of the reverse step into the overall rate naturally becomes larger when the reaction is closer to equilibrium. As a result, the temperature dependence of the overall rate becomes more complex than predicted by a single Arrhenius equation.

The aforementioned observations of the nonlinear Arrhenius plots can be generalised mathematically by taking the isoconversional derivative [58,63] of the rate (Equation 22).

This procedure gives rise to the isoconversional activation energy:

$$E_\alpha = -R\left[\frac{\partial \ln(d\alpha/dt)}{\partial T^{-1}}\right]_\alpha \qquad (26)$$

where the subscript α denotes values related to a given conversion. The application of this procedure to the rate equations of multi-step processes permits establishing a link between the effective activation energy of the overall process and the activation energies and other parameters of the individual steps. As discussed elsewhere [58,63] establishing such link allows one to understand variable activation energy as a frequently observed experimental phenomenon and as a theoretical concept. The latter was introduced some twenty years ago by Vyazovkin [8,64] who argued that one normally measures the overall kinetics determined by the rate of more than one step. Consequently, the experimentally determined activation energy is an effective (global, apparent, composite) parameter, whose value depends on the values of the parameters of the individual steps and may vary when the relative contributions of the steps to the overall process rate change with temperature or/and conversion [8,64].

Substitution of P_0 from Equation (23) into Equation (22) followed by taking the isoconversional derivative leads to [51]:

$$E_\alpha = E_1 - R\left[\frac{\partial \ln(1-(P/P_0))}{\partial T^{-1}}\right]_\alpha = E_1 + \Delta H^0 \frac{P}{P_0 - P} \qquad (27)$$

where E_1 is the activation energy of the forward reaction. Equation (27) predicts the effective activation energy to be temperature dependent because of the temperature dependence of P_0 (Equation 23). The resulting temperature dependence of E_α affords explaining some basic effects of temperature and pressure on experimentally measured values of the activation energy. Let us start by noting that for reversible endothermic decomposition such as decomposition of carbonates or dehydration of inorganic hydrates ΔH^0 and the whole second addend in Equation (27) is positive. It means that the experimentally measured activation energy of such processes should generally overestimate the value of the activation energy for the forward reaction. Obviously, the magnitude of overestimating should depend on temperature as well as on the applied partial pressure (P).

3.2. Effect of temperature

The effect of temperature on the experimental activation energy boils down to the temperature dependence of the pressure term in Equation (27). This dependence is presented in Figure 2 for decomposition of calcium carbonate. It is seen that when decomposition proceeds at temperature close to the equilibrium value T_0, i.e. when P_0 is close to P, the pressure term can take on very large values and so can the effective activation energy. Nonetheless, when decomposition is carried out at temperatures significantly larger than T_0, i.e. when P_0 exceeds significantly P, the pressure term tends to zero so that the effective activation energy becomes similar to the activation energy of the forward process. Note that a similar trend is predicted by other more complex models of reversible decompositions [8,65–67].

The temperature effect predicted by Equation (27) is also consistent with the afore-discussed nonlinear Arrhenius plots (Figure 3). Indeed, an increase in the Arrhenius plot

slope with decreasing temperature is equivalent to an increase in the effective activation energy. It should be emphasised that obtaining the nonlinear Arrhenius plots requires performing multiple isothermal experiments in a broad range of temperatures, including the temperatures close to T_0. The use of the temperatures close to T_0 is critical in detecting the nonlinearity because it is more pronounced in that temperature region (Figure 3). However, conducting isothermal experiments near T_0 provides a significant challenge because decomposition becomes extremely slow. It is much easier to carry out nonisothermal runs and apply an isoconversional method to the obtained data. In this case, the nonlinearity of the Arrhenius plot is readily detected as the temperature dependence of the effective activation energy.

Isoconversional methods have now become a major tool for kinetic analysis of data generated by thermal analysis techniques such as TGA and DSC. Although there are a plenty of isoconversional methods, we are not going to discuss their details especially that they have been overviewed elsewhere [9,58,68]. It needs only to be stressed that all these methods, albeit with different accuracy, enable the effective activation energy to be determined as a function of conversion. What is more important is that in nonisothermal runs one can typically explore decomposition in a much broader temperature range than in isothermal runs. As one would expect, the broader the temperature range the easier to detect a variation in the effective activation energy.

Since in nonisothermal experiments conversion is linked to temperature, one can readily convert the isoconversional E_α vs. α dependence into a dependence of the E_α on T [63]. Isoconversional kinetic analysis requires collecting α vs. T data at different temperature programmes, e.g. at different heating rates. With increasing the heating rate the same conversion is reached at a larger value of T_α. The set of the T_α values obtained at different heating rates is then used to estimate the mean temperature for each value of α. Replacing the values of α with the respective mean temperatures converts the E_α vs. α dependence into a dependence of E_α on T. Therefore, the E_α vs. α and E_α vs. T dependencies are equivalent to each other so that the reasoning used to explain the temperature dependence of the effective activation energy can be used to explain the corresponding conversion dependence.

Isoconversional methods have been routinely applied to reversible decompositions and the resulting conversion dependencies E_α vs. α are frequently encountered in the literature. Perhaps, the most common case being the thermal dehydration of inorganic hydrates. The E_α values for this process typically decrease with conversion and/or temperature. Examples of such effects include the thermal dehydration of $CaC_2O_4 \cdot H_2O$ [53,69–72], $Li_2SO_4 \cdot H_2O$ [51,54,73,74], $CaSO_4 \cdot 2H_2O$ [53,75], $Ni_3(PO_4)_2 \cdot 8H_2O$ [76], $NiC_2O_4 \cdot 2H_2O$ [77], $La_2(C_2O_4)_3 \cdot 10H_2O$ [78], $La_2(CO_3)_3 \cdot 3.4H_2O$ [79].

Figure 4 presents the results of isoconversional analysis of TGA and DSC data on dehydration $CaC_2O_4 \cdot H_2O$ in a broad range of heating rates, 0.3–20°C min^{-1} [53]. The resulting E_α vs. α dependencies have been estimated by means of an advanced isoconversional method [72] and converted to the E_α vs. T dependencies shown in Figure 4. It is seen that all dependencies follow the same descending trend, which is exactly the trend predicted by Equation (27) for the effect of temperature. That is, the effective activation energy should decrease with increasing temperature and ultimately reach the activation energy of the forward reaction. In agreement with this effect the E_α values at lowest temperatures are nearly twice larger than at the highest ones. At the highest temperatures the E_α values
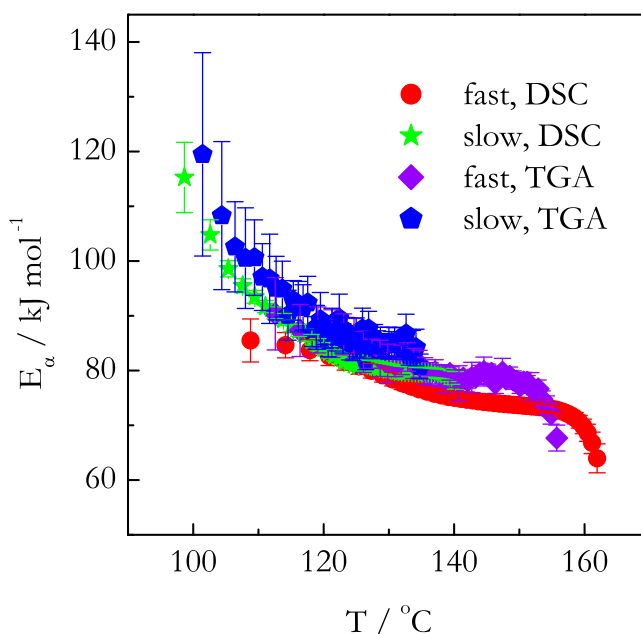
Figure 4. Isoconversional activation energies for thermal dehydration of calcium oxalate monohydrate studied by TGA and DSC. 'slow' and 'fast' represents respectively the heating rate ranges 0.75–2.5 and 5–20°C min^{-1}. Reprinted with permission from Liavitskaya and Vyazovkin [53]. Copyright 2017 American Chemical Society.

reach roughly 70 kJ mol^{-1} that can serve as an estimate for the activation energy of the forward reaction. Within the typical uncertainty this value agrees well with 65 kJ mol^{-1}, reported by Dollimore et al. [80] for this process in vacuum, i.e. under the conditions when the reverse reaction is suppressed.

In addition, Figure 4 suggests that under the nonisothermal conditions the use of faster heating rates allows one to obtain the effective activation energies that approach closer the activation energy for the forward reaction. Of course this is just another manifestation of the temperature effect. Faster heating rates shift the process to higher temperatures, i.e. further from equilibrium. Therefore, for obtaining kinetic parameters for the forward reaction under ambient pressures one can be advised to employ the fastest heating rates. When doing that one should be mindful of the ICTAC recommendations [81] to avoid the heat transfer problems. In connection with employing faster heating rates, there appears to be a great potential for recently commercialised [82] technique of fast scanning calorimetry [83] that is yet to be applied for kinetic studies of reversible decompositions.

3.3. Effect of partial pressure

In addition to the discussed temperature effect, which manifests itself via the temperature dependence of P_0, the effective activation energy is affected by the partial pressure, P of the product gas. It is obvious from Equation (27) that under vacuum, i.e. when $P \rightarrow 0$, the effective activation energy approaches the value of the activation energy of the forward reaction. This effect is expected because lowering the partial pressure decreases the rate of the reverse reaction (see Equation 5) so that the overall rate of reversible decomposition

approaches the rate of the forward reaction. This explains an advantage of applying high vacuum when studying the kinetics of reversible reactions.

Equation (27) suggests that an increase in the partial pressure of the gaseous product increases the effective activation energy of the reversible decomposition. This effect is also revealed in Figure 3. It is seen that for the same temperature range the slope of the Arrhenius plots increases with increasing the partial pressure. This means that an increase in the activation energy should be accompanied by an increase in the preexponential factor. Some representative examples of this effect are the studies of Dollimore et al. [80] on dehydration calcium oxalate monohydrate and of Koga et al. [46] on decomposition of calcium hydroxide. In the case of calcium oxalate monohydrate dehydration the activation energy has been found to increase from 65 kJ mol^{-1} in vacuum to 200 kJ mol^{-1} under 1310 Pa of water pressure. The respective values of the preexponential factor have similarly been found to increase drastically, i.e. $\sim 10^{18}$ times. For calcium hydroxide decomposition, raising the partial pressure of water from 650 to 5650 Pa has caused the isoconversional activation energy to roughly double (from ~ 300 to ~ 600 kJ mol^{-1}) and the preexponential factor to increase about 10^{17} times.

Maciejewski and Baldyga [84] have reported a dramatic effect of the partial pressure of carbon dioxide on the decomposition kinetics of the calcium carbonate decomposition. In vacuum, the activation energy of the process has been around 200 kJ mol^{-1}. At the partial pressures of carbon dioxide 2000, 4000, and 6000 Pa the effective activation energies have been estimated respectively as ~ 280, 360, and 440 kJ mol^{-1}. The experiments have been conducted in the temperature region 1018–1048 K. With this information at hand we can try to use Equation (27) to simulate the effective activation energies for decomposition of calcium carbonate at the above pressures. To do that we assume that the activation energy for the forward reaction in Equation (27) is 200 kJ mol^{-1} (i.e. the value obtained under vacuum) and that the equilibrium pressure varies with temperature according to Equation (24). For ΔH^0 we use 178 kJ mol^{-1} [85].

The results of the simulation are displayed in Figure 5. As discussed earlier, the effective activation energy decreases with temperature. This trend holds for all partial pressures, although the temperature dependence becomes stronger when applying higher pressures. Likewise, for any given temperature the effective activation energy increases dramatically with increasing the partial pressure. It is noteworthy that the effective activation energies determined experimentally by Maciejewski and Baldyga [84] and the theoretical values predicted by Equation (27) are quite consistent with each other. In other words, Equation (27) can be used for reasonable quantitative evaluations.

Examples of an increase in the effective activation energy with increasing the partial pressure of the gaseous product are commonly found in recent literature. Avila et al. [86] have studied decomposition of limestone under flowing air containing 0 and 15% of carbon dioxide and found that the activation energy in the presence of carbon dioxide increased about two times. Even larger difference has been observed by Tian et al. [52] for the nonisothermal decomposition of limestone in the mixture containing 21% of oxygen and 79% of carbon dioxide relative to the mixture containing 79% of nitrogen instead of carbon dioxide. Two to three times bigger values of the activation energy have been determined by Reyes-Martinez et al. [87] for dehydration of a series of compounds M(H2O)2[Ni(CN)4]·nH2O (M = Ni, Co, Mn; n = 1, 2, 4) in air containing 3130 Pa of water relative to dry air.
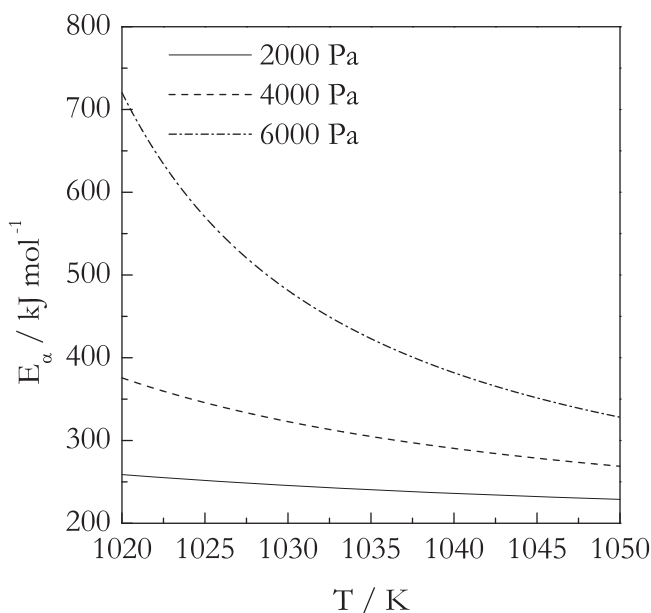
Figure 5. Temperature dependence of the effective activation energy for decomposition of calcium carbonate at different partial pressures of carbon dioxide simulated by Equation (27).

In agreement with the above pressure effects, Catti et al. [42] have found that raising the partial pressure of hydrogen causes an increase in the activation energy and preexponential factor of dehydrogenation of some complex metal hydride systems. Perejon et al. [50] too have reported a significant increase in the activation energy of dehydrogenation of magnesium hydride with increasing the partial pressure of hydrogen (Figure 6). The values obtained at 10 and 20 bar hydrogen pressure are markedly larger than the value $117\pm7\,kJ\,mol^{-1}$ obtained under $5\cdot10^{-8}$ bar vacuum. However, it has been demonstrated that explicitly introducing the pressure term (Equation 4) into the isoconversional equation of Friedman [88] as follows:

$$\ln\left(\frac{d\alpha}{dt}\right)_\alpha - \ln\left(1 - \frac{P}{P_0}\right) = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_\alpha} \tag{28}$$

allows for obtaining the activation energies that are independent of pressure. The resulting values $124 \pm 7\,kJ\,mol^{-1}$ and $127 \pm 4\,kJ\,mol^{-1}$ for 10 and 20 bar respectively agree within the uncertainty with value obtained from the vacuum runs. In spite of this, the application of a similar approach (Equation 28) to decomposition of calcium hydroxide under different water pressures has still resulted in the values of the activation energy that increased with pressure [46]. In order to remedy the issue, Koga et al. [46] have proposed a more complex pressure term. Its use has permitted describing the process with a single set of the Arrhenius parameters in the range of partial pressures of water 0.65–5.59 kPa. Therefore, accounting for a pressure term generally provides an opportunity for evaluating the kinetics of the forward reaction. An advantage of this approach is that it does not involve experimental efforts associated with reducing the rate of the reverse reaction, such as employing very low pressures or fast heating rates. Of course, its use requires
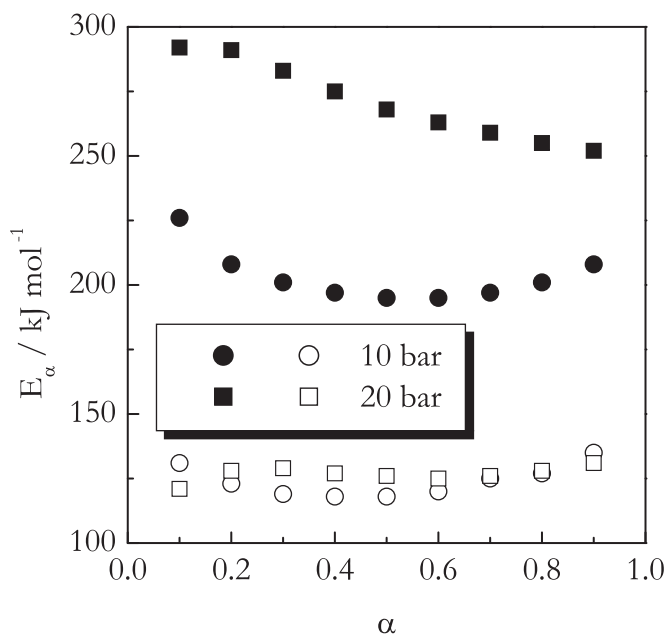
Figure 6. Isoconversional activation energies for dehydrogenation of magnesium hydride [50]. Solid symbols represent the estimates obtained without accounting for the pressure term. The values estimated with account of the pressure term (Equation 28) are shown as open symbols.

knowledge of the temperature dependence of the equilibrium pressure. The dependence can be estimated subject to availability of the thermodynamic parameters (Equation 23).

In principle, pressure independent Arrhenius parameters can be extracted from the pressure dependent rate data by using the methods of nonparametric kinetics, i.e. without assuming any particular form of the pressure term [89]. This approach follows the original method by Serra et al. [90] that makes use of singular value decomposition of the rate matrix data into two vectors that represent respectively the temperature and conversion dependence of the rate. Deutsch et al. [89] have expanded this method to pressure dependent rate data so that one can isolate pressure independent temperature dependence and fit it to the Arrhenius equation. This approach has been applied to evaluate pressure independent Arrhenius parameters for reversible processes of decomposition of $CdCO_3$ [89] and of oxidation of Cu_2O to CuO [91].

In their study of $LiBH_4$ decomposition under different hydrogen pressures, Pendolino et al. [47] have made an attempt to account for the pressure effect to estimate the activation energy of the forward reaction by using the Kissinger [92,93] method. In this method, the effective activation energy is evaluated as

$$E_{ef} = -R\frac{d\ln(\beta/T_p^2)}{dT_p^{-1}} \tag{29}$$

where β is the heating rate and T_p is the peak temperature as measured by DSC. The effect has been accounted for by using the pressure dependent form of the effective activation

energy derived by Reading et al. [21]:

$$E_{ef} = E_1 - RT \ln \left(1 - \frac{P}{P_o} \right) \tag{30}$$

A problem here is that Equation (30) does not appear to have been derived properly. It has been arrived at as follows [21]. First, an equation for the rate constant for the forward reaction, k_f, has been obtained. Upon adjustment to the notations used in the present paper, it can be written in the following form:

$$k_f = A \exp \left[-\frac{E_1 - RT \ln(1 - (P/P_o))}{RT} \right] \tag{31}$$

Then, the effective activation energy (Equation 30) has been determined 'by comparison with the usual form of the Arrhenius equation' [21]. It can be demonstrated that this idea would give the correct result if the subtrahend in the numerator of Equation (31) were temperature independent. In the general case, however, the activation energy should be determined as the logarithmic derivative of the rate constant with respect to reciprocal temperature. It means that the effective activation energy derived from Equation (31) is:

$$E_{ef} = -R \frac{d \ln k_f}{dT^{-1}} = E_1 - R \frac{d \ln(1 - (P/P_0))}{dT^{-1}} = E_1 + \Delta H^0 \frac{P}{P_0 - P} \tag{32}$$

The result obtained is the same as that given by Equation (27). This is not surprising because k_f introduced by Equation (31) is nothing else but the effective rate constant from Equation (25).

It must be emphasised that Equation (32) as well as Equation (27) predicts the pressure dependence of the activation energy that differs dramatically from the one predicted by Equation (30). Examples of the latter are presented in Figure 7 for the process of decomposition of calcium carbonate. The dependencies have been computed by Equation (30) to imitate the experimental measurements by Maciejewski and Baldyga [84], i.e. the same way as the dependencies presented in Figure 5. Namely, the E_1 value has been set to be 200 kJ mol^{-1} and Equation (24) has been employed for the temperature dependence of the equilibrium pressure. Clearly, Equation (30) predicts a very weak dependence on the partial pressure. It is much weaker than the one predicted by Equation (27), and the resulting values of the activation energy are definitely inconsistent with the actual values measured experimentally by Maciejewski and Baldyga [84]. This is yet another indication that Equation (30) does not account for pressure correctly.

Agresti [48] has proposed a different approach to accounting for the pressure term within the formalism of the Kissinger method. This approach makes use of Equation (22) to derive an equation for the temperature dependence of $\ln(\beta/T_p^2)$. The resulting equation is quite complex and predicts a nonlinear dependence for the Kissinger plots of $\ln(\beta/T_p^2)$ against $(1/T_p)$. Although no explicit expression for the effective activation energy has been derived, its temperature and pressure dependencies can be figured out from the slopes of the Kissinger plots simulated for decomposition of MgH$_2$ [48]. Since the shape of the plots is similar to that of the nonlinear Arrhenius plots presented in Figure 3, one can conclude that they suggest the same trend for the effective activation energy. That is, the effective activation energy decreases with increasing temperature and increases with increasing partial pressure.
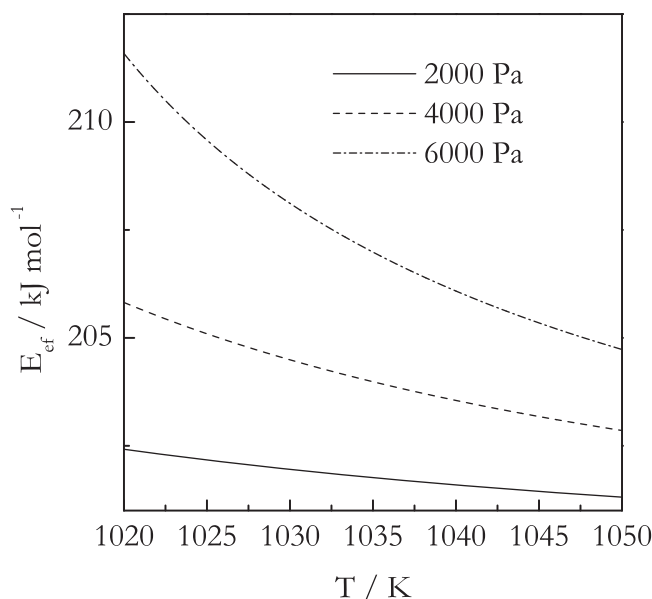
Figure 7. Temperature dependence of the effective activation energy for decomposition of calcium carbonate at different partial pressures of carbon dioxide simulated by Equation (30).

3.4. Further effects of pressure

As we can see the use of the simple pressure term (Equation 4) in the rate equation (Equation 22) makes it possible to predict correctly basic effects of pressure on the kinetics of reversible decomposition. Nonetheless, its practical use may require some empirical adjustments. One such adjustment is the use of the power function of Equation (4) [20,53,91,94,95]:

$$h(P) = \left(1 - \frac{P}{P_o}\right)^n \tag{33}$$

where n is larger than 1. In its simplest form ($n = 1$) the pressure term describes a decelerating dependence of the rate on equilibrium pressure. However, at n larger than 1 this dependence becomes autocatalytic, i.e. the rate passes through a maximum. That is, the use of the pressure term in the form of Equation (33) expands its application range to a broader range of the decomposition kinetics. Another adjustment is associated with accounting for the fact that at a given temperature P_0 does not reach instantaneously its equilibrium value determined by Equation (23). Rather, it builds up, i.e. increases at a finite rate in proportion to the extent of conversion, α. This can be accounted for by replacing P_0 with adjusted equilibrium pressure [53]:

$$P_0' = \alpha^n P_0 \tag{34}$$

where n is an empirical exponent that describes the strength of the pressure dependence on conversion. Accounting for the pressure buildup has played the crucial role in understanding the difference in the kinetics of reversible decomposition occurring during continuous heating and cooling, respectively [53].

It should be stressed that sometimes the actually observed pressure effects disagree with the normal expectations discussed in sections 3.2 and 3.3. For instance, Nahdi et al. [96] have observed that for dehydroxylation of kaolinite the activation energy decreases from 233 ± 15 to $188 \pm 10 \, \text{kJ mol}^{-1}$ when the partial pressure of water is raised from 0.1 to 500 Pa. This is evidently inconsistent with the typical effect of the partial pressure discussed earlier. The observation has been explained by a change in the rate limiting step from dehydroxylation to desorption of water.

Another intriguing example is found in a study of decomposition of synthetic malachite ($Cu_2CO_3(OH)_2$) by Koga et al. [97,98]. The compound decomposes with a release of two gases, H_2O and CO_2. Contrary to what one would expect for reversible decomposition, improving the efficiency of removal of the forming gases by increasing the flow rate of nitrogen or by applying vacuum has resulted in shifting the process to higher temperatures. Considering that increasing the partial pressure of CO_2 had been known [99] to shift decomposition of this compound to higher temperature, it has been inferred [97] that the released water may catalyse the process. Further kinetic study in different gaseous atmospheres has clarified the situation. The resulting Arrhenius parameters for different conditions are presented in Figure 8. It is seen that in vacuum and N_2 flow, i.e. when the generated product gases are efficiently removed, the activation energy is around $190 \, \text{kJ mol}^{-1}$. Under the flow of CO_2 the activation energy rises to $335 \, \text{kJ mol}^{-1}$ as expected for reversible decomposition under elevated pressure of the gaseous product. In the presence of water vapour, the activation energy drops to $167 \, \text{kJ mol}^{-1}$ as one would expect in the case of catalysis. Finally, under the self-generated atmosphere (SGA) formed inside a crucible sealed with a pierced lid the activation energy takes on a value $224 \, \text{kJ mol}^{-1}$, which appears to indicate that under such conditions the decelerating effect of CO_2 outweighs the accelerating action of H_2O.

The accelerating effect of increasing partial pressure of the product water vapour has also been reported for decomposition of zinc carbonate hydroxide [100] and sodium hydrogencarbonate [101]. Both compounds decompose with simultaneous release of CO_2 and H_2O. Although introduction of CO_2 into the gaseous atmosphere reveals no detectable effect on the decomposition rate of both compounds, the rate is markedly accelerated by increasing the water vapour pressure. Remarkably, the accelerating effect manifests itself differently for these compounds. If in zinc carbonate hydroxide the acceleration correlates with a decrease in the activation energy, for sodium hydrogencarbonate it is associated with an increase in the preexponential factor.

It is well known [12] that the processes involving a reversible step can demonstrate an anti-Arrhenian temperature dependence (the rate decreases with increasing temperature) that gives rise to a negative value of the effective activation energy. The simplest reaction pathway that may reveal such an effect is a reversible step followed by an irreversible one. A detailed analysis of the reaction pathways yielding negative activation energies has been given elsewhere [102]. Generally, it happens when the pathway includes an intermediate product whose enthalpy of formation from the preceding step reactants exceeds the activation energy of the following reaction step [102]. Recently, Valverde et al. [20,49] have reported negative values of the effective activation energy for the thermal decomposition of $CaCO_3$. The phenomenon has been observed near equilibrium ($P/P_0 \geq 0.7$ and $T > 830°C$) and explained by invoking a reversible step of the structural transformation of the metastable CaO intermediate.
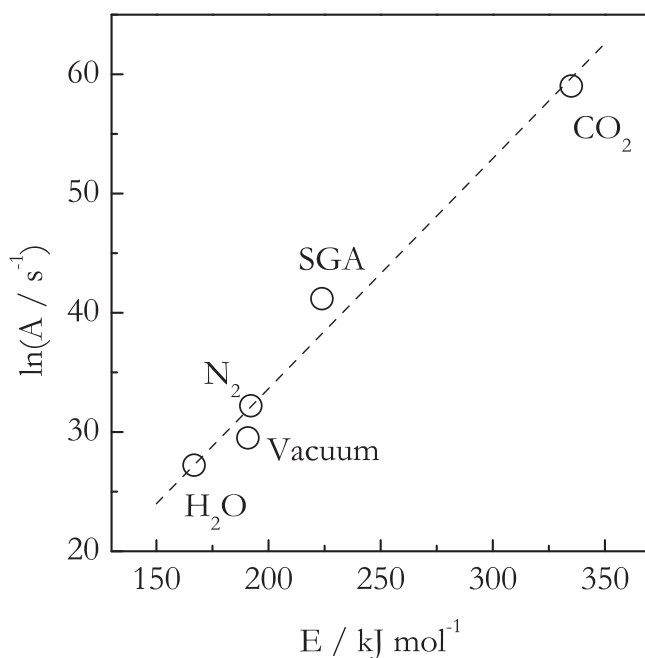
Figure 8. Preexponential factors and activation energies for decomposition of synthetic malachite in different gaseous atmospheres [97].

4. Pressure induced by diamond anvil cell and inert gas

In his book, van 't Hoff mentions [103] that the decomposition temperature of solid copper calcium acetate hexahydrate decreases from 78 to 40°C when pressure is raised from ambient to 1000 atm. The effect has been linked to the fact that the conversion of the solid reactant to products is accompanied by a decrease in volume. This idea finds its modern reflection in the theory of the activated complex [104]. According to this theory the isothermal derivative of the rate constant with respect to pressure yields the so-called volume of activation, $\Delta V^{\neq}$:

$$\left(\frac{\partial \ln k}{\partial P} \right)_T = -\frac{\Delta V^{\neq}}{RT} \tag{35}$$

By its meaning this value is the difference between the volume of the activated complex and reactant. Indeed, if the volume decreases ($\Delta V^{\neq}$ is negative), the reaction is accelerated with increasing pressure. Conversely, if $\Delta V^{\neq}$ is positive, increasing pressure slows the reaction down.

A change in pressure affects the values of experimentally estimated activation energy and preexponential factor. For example, the activation energy takes the following form [104]:

$$E = \Delta H^{\neq} - P\Delta V^{\neq} + RT \tag{36}$$

where $\Delta H^{\neq}$ is the activation enthalpy. Equation (36) permits some useful estimates regarding the pressure effect. For decomposition under ambient pressure the order of magnitude for E and $\Delta H^{\neq}$ is 10^5 J mol^{-1}. On the other hand, the magnitude of the $\Delta V^{\neq}$ values

is around 10^{-5} m^3 mol^{-1} [105]. It means that any significant changes in the activation energy should generally be expected when pressure rises to the level of GPa. Processes under such pressures are explored routinely by using diamond anvil cells in combination with spectroscopic methods [106].

Studies of the decomposition kinetics in diamond anvil cells are not very common. One should note a work of Miller et al. [107,108] on 1,3,5-trinitrohexahydro-l,3,5-triazine (RDX). They have found that $\Delta V^{\neq}$ is negative for the α form of RDX and its decomposition accelerates with increasing pressure. However, for the pressure range 1.4–2.1 GPa the activation energy has been constant (~ 210 kJ mol^{-1}) within the experimental uncertainty. The same authors [109] have additionally studied the thermal decomposition kinetics of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). In this study the activation energy has decreased dramatically from 500 to 150 kJ mol^{-1} with an increase in pressure from 3.6–6.5 GPa. The process has been determined to have a positive value of $\Delta V^{\neq}$ so that its rate decreased with increasing pressure. It should be noted that the deceleration has been due to a decrease in the value of the activation entropy, i.e. of the preexponential factor. Glascoe et al. [110] have employed a diamond anvil cell to probe the decomposition kinetics of HMX in a broader range of pressures: 10^{-4} (ambient pressure) – 3.6 GPa. The results obtained indicate that the process decelerates only above 0.1 GPa. At lower pressures the decomposition accelerates with increasing pressure that has been explained as an autocatalytic action of the decomposition gases.

The above examples illustrate the effect of pressure on thermally initiated decomposition, i.e. decomposition induced by increasing temperature. Yet, decomposition of solids can be induced at ambient temperature by increasing diamond anvil pressure alone. Examples of such processes are quite rare. One of them is decomposition of KHSO$_4$ to K$_3$H(SO$_4$)$_2$ and H$_2$SO$_4$ that becomes detectable by Raman spectroscopy when pressure is raised to 0.4 GPa [111,112]. Another is decomposition of H$_3$BO$_3$ to HBO$_2$ and H$_2$O [113,114]. The process has been detectable by XRD and Raman spectroscopy at pressure of 5.4 GPa [113]. A lower pressure threshold of ~ 2 GPa has been established in a later synchrotron XRD study of this process [113]. Pressure-induced decomposition is generally expected to occur in solids, for which the volume of the product phase is smaller than that of the original solid. However, as posited by Arora [115], decomposition rarely happens at ambient temperature because the growth of the product phase nuclei is kinetically hindered by a large activation energy barrier. As a result, one is more likely to encounter pressure induced amorphization.

More commonly the decomposition kinetics under pressure is studied by using high pressure DSC and TGA instruments. These instruments are pressurised by a compressed gas and typically work at pressures not exceeding 10–15 MPa. Similarly, they can be used for studies under reduced (sub-ambient) pressures. When pressure is controlled by an inert gas, the pressure effects on the kinetics are not nearly as straightforward as in the case of using a product gas. The latter is simply a reactant in the reverse reaction. For this reason, the kinetic effect of the product gas pressure originates from a change in the thermodynamic driving force, as discussed earlier. In its turn, an inert gas does not react either with the products or with the reactant (cf. Equation 2). This means it cannot affect the thermodynamic driving force of the process. Thus, from the thermodynamic standpoint, the presence of an inert gas should not affect the rate of reversible decomposition. Nevertheless, this is not true from the kinetic standpoint. The rate of reaching equilibrium

does depend on the gaseous environment in general. If a solid decomposes in vacuum, the product gas molecules can leave the surface without any resistance from the gaseous environment. Conversely, if the environment is an inert gas, the product gas molecules face collisional (diffusional) resistance from the gaseous environment that should cause deceleration of reversible decomposition. The resulting deceleration can be quite dramatic as seen, for example, from comparison of the rates of reversible decomposition of titanium hydride under vacuum and helium [11].

In more general terms, the presence of an inert gas makes the product gas molecules to stay longer in the reaction zone. As a result, the product gas acquires a greater chance to engage in a reaction with either the products or the reactant itself. A reaction between the product gas and the reactant can lead to autocatalysis and, thus, to acceleration of decomposition. Acceleration is yet another effect that an inert gas pressure may have on decomposition of solids.

To better understand the specifics of the kinetics in the presence of an inert gas one can draw an analogy with the Stefan flow [116–118]. This is a phenomenon of vapour flowing away from the liquid surface under pressure of an inert gas. In this circumstance, the simplest form of the equation that describes the rate of evaporation is as follows [116]:

$$v = \frac{D}{h} \ln \left(\frac{P_{\text{tot}}}{P_{\text{tot}} - P} \right) \tag{37}$$

where D is the diffusion coefficient, h is the distance from the liquid surface, P is the partial pressure of vaporising liquid, and P_{tot} is the total pressure that includes both P and the pressure of an inert gas. Equation (37) predicts two important effects. First, the rate decreases with increasing the total pressure and, thus, the pressure of an inert gas. This seems self-obvious. The higher pressure means denser environment and, thus, higher resistance to the product gas flow. Second, the rate decreases with decreasing the diffusion coefficient. This means that for the same product gas its flow rate depends on the nature of the inert gas that makes up the gaseous environment.

The use of the molecular kinetic theory of gases has allowed Sutherland [119] to arrive at the following equation for the diffusion coefficient:

$$D \propto \frac{T^{3/2}}{P_{\text{tot}}(a_1 + a_2)^2} \sqrt{\frac{1}{m_1} + \frac{1}{m_2}} \tag{38}$$

where a_1 and a_2 are the radii and m_1 and m_2 are the masses of molecules. Equation (38) formalises the intuitively expected effect of the inert gas nature, viz., heavier and larger molecules of the gaseous environment should exert stronger resistance to the product gas flow. The effect of the surrounding gas nature is quite strong. For instance, when switching from hydrogen to nitrogen environment the diffusion coefficient decreases ~ 4 times for dichlorodifluoromethane [120] and ~ 3 times for water [121]. Even larger decrease (~ 5 times) is observed for diffusion of the latter when switching from hydrogen to carbon dioxide [121]. On the other hand, switching the atmosphere between the gases of similar molecular masses such as nitrogen, oxygen, and air has no significant effect on the diffusion coefficients of a wide variety of gases [122]. Another kinetically relevant effect suggested by Equation (38) is that the diffusion rate decreases in direct proportion to an increase in the total pressure. The effect has been confirmed by multiple experimental studies, see

Jost [123], Takahashi and Hongo [124], Carreon-Calderon and Uribe-Vargas [125], and references therein.

The aforementioned effects are of relevance in the case of reversible decomposition. It means that the factors that slow down the forward reaction, i.e. a decrease in the coefficient of diffusion in general and an increase in the total pressure in particular should slow down the overall rate of reversible decomposition and, thus, shift it to higher temperature. There are several publications that demonstrate that increasing the molecular mass of the inert gas shifts reversible decomposition to higher temperature. Criado and Trillo [126] have found that decomposition of $CaCO_3$ under nitrogen occurs $\sim 50°C$ higher than under helium. They have additionally demonstrated that no such effect is observed for the irreversible decomposition of nickel formate. Later, Reich et al. [127] have reported that decomposition of $CdCO_3$ in argon takes place about 15°C higher than in nitrogen. The effect has been further illustrated by Maciejewski [128], who studied decomposition of $CaCO_3$ under helium, nitrogen, argon, and krypton. The decomposition temperature has increased systematically with increasing the molecular mass of the inert gas. The temperature difference between the decomposition under the lightest and heaviest gas has been $\sim 50°C$. The deceleration is even more obvious when decomposition is studied under isothermal conditions. Figure 9 displays kinetic curves for decomposition of $CaCO_3$ under helium, nitrogen, and krypton. The measurements have been carried out at the same temperature (620°C) and inert gas pressure (10 kPa). It is seen that the rate of decomposition slows down markedly with increasing the molecular mass of the inert gas used. For example, reaching 50% decomposition ($\alpha = 0.5$) takes about 2.5 times longer under krypton than under helium.

Naturally, any significant deceleration of reversible decomposition under inert gas pressure can be expected to reveal itself in substantial changes in the Arrhenius parameters. Surprisingly, until recently [129] there have been no adequate kinetic studies to probe such effect. The only pertinent result was that by Reich et al. [127], who found that the activation energy remains unchanged when switching from nitrogen to argon. Unfortunately, the result is marred by two flaws. First, it was obtained by using single heating rate methods that are presently known [9,130] to be unreliable. Second, no values of the preexponential factors were reported so that there was no way to know whether this parameter was affected by molecular mass of an inert gas.

As already discussed, an increase in an inert gas pressure should decelerate reversible decomposition and shift it to higher temperature, if the process is studied under non-isothermal conditions. This effect has been observed for reversible decomposition of semi-clathrate hydrates [131,132]. A high pressure DSC work of Sugahare et al. [131] has demonstrated that for tetra–n–butyl ammonium bromide semi-clathrate hydrate the decomposition temperature increases by $\sim 5°C$ with increasing the pressure of tetrafluoromethane from 0.1 to 79 MPa. It has been proved spectroscopically that tetrafluoromethane does not participate in the formation semi-clathrate hydrate. Similar results have been obtained by Shimada et al. [132] for decomposition of tetra-n-butylphosphonium acetate semi-clathrate hydrate pressurised by ethane. However, the increase has been $\sim 1°C$ per increase in pressure from 0.1–3.1 MPa.

Nevertheless, an opposite effect is observed [133] for dehydration reactions of the three minerals: mascallisterite, inderite, and kurnkovite run under elevated pressure of nitrogen. All three minerals have shown a decrease in the decomposition temperature by a few
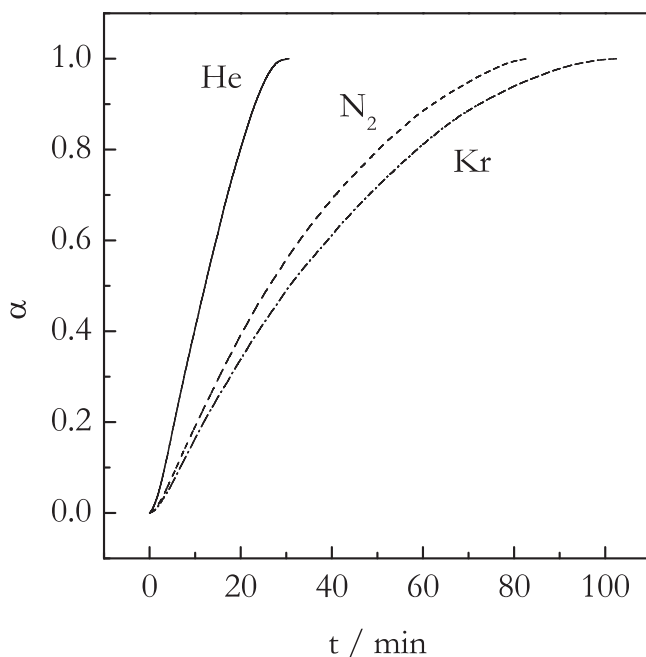
Figure 9. Decomposition of calcium carbonate at 620°C under 10 kPa pressure of different inert gases (helium: solid line; nitrogen: dash line; krypton: dash-dot line). The purity of gases 99.995%. The data were collected by using TGA (Mettler-Toledo TA-2000C) on 20 mg samples placed in platinum crucibles. The data is courtesy of Dr. Maciejewski.

degrees upon increasing the nitrogen pressure from 1 to 4 MPa. It is worthy of note that for inderite this temperature has been at least 10°C lower than under an ambient pressure (0.1 MPa) of flowing nitrogen [134]. No explanation to this effect has been proposed [133]. Perhaps, water vapour produced during decomposition of these compounds has an autocatalytic action similar to that reported by Koga et al. for decomposition of hydroxides [97,98,100,101].

Only recently an adequate study of the effect of inert gas pressure on the Arrhenius parameters of reversible decomposition have been conducted by Stanford et al. [129]. By introducing the Arrhenius type of temperature dependence for the diffusion coefficient into Equation (38), they have proposed that the effective rate constant of reversible decomposition under pressure of an inert gas should have the following form:

$$k_{ef} = \frac{A}{P_{tot}} \exp\left(-\frac{E_D + E}{RT}\right) \tag{39}$$

where E_D is the activation energy of the product gas flow in an inert gas environment. Equation (39) suggests that under pressure of an inert gas the effective activation energy should be larger than the activation energy of the forward reaction by the value of E_D. On the other hand, the effective preexponential factor should become smaller than that for the forward reaction by the factor equal to the value of the total pressure. Considering that for diffusion of gases in gases the E_D value is usually around 4–6 kJ mol^{-1} [58,120,129] and that the E value is typically around 100 kJ mol^{-1} or more, a contribution of E_D to the
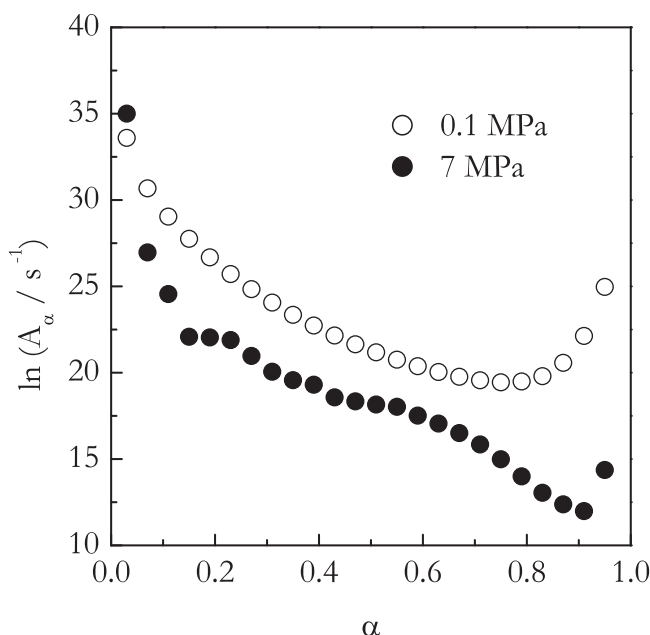
Figure 10. Isoconversional preexponential factors for lithium sulfate monohydrate dehydration under different pressures (open circles 0.1 MPa, solid circles 7 MPa). Reprinted with permission from Stanford et al. [129]. Copyright 2019 American Chemical Society.

effective activation energy is likely to be comparable to the experimental uncertainty. That is, the deceleration of reversible decomposition due to an increase in an inert gas pressure should be associated primarily with a decrease in the preexponential factor.

The effect predicted by Equation (39) has been confirmed by a high pressure DSC study of the thermal dehydration of lithium sulfate monohydrate [129]. An increase in nitrogen pressure from 0.1 to 7 MPa has caused the process temperature to increase by more than 10°C. The isoconversional activation energy of the process has been practically unaffected by the pressure increase, whereas the $\ln A_\alpha$ values have decreased on average by 4.5 ± 0.6 (Figure 10). It has also been suggested [129] that the effect of the molecular mass of an inert gas should be expected to reveal itself primarily via a change in the preexponential factor. More specifically, the value of the latter should decrease with increasing the molecular mass.

For autocatalytic decomposition one should generally expect an increase in pressure of an inert gas to accelerate the process and, thus, to lower its temperature. As explained earlier, the presence of an inert gas should slow down the escape of products from the reaction zone that would increase a chance of their reaction with the decomposing reactant. Autocatalysis is frequently encountered in decomposition of explosives and propellants that tend to produce highly reactive decomposition products such as NO and NO_2. The already discussed study [110] on HMX decomposition in a diamond anvil cell is one example of such effect. Relatedly, a high pressure DSC work by Burnham et al. [135] has found that the decomposition temperature of HMX drops by 20°C upon increasing the nitrogen pressure from 0.1 to 7 MPa. Yi et al. [136] have examined the decomposition kinetics

of two double base propellants containing 3,6-bis(1H-1,2,3,4-tetrazol-5-yl-amino)-1,2,4,5-tetrazine under nitrogen pressures of 0.1, 4, and 7 MPa. The decomposition temperature has decreased with increasing pressure by about 5°C. The observed acceleration correlates with a decrease in the activation by about 40 kJ mol^{-1} that is partially offset by a decrease in the preexponential factor from roughly 10^{19} to 10^{15} s^{-1}. The effects of a similar magnitude are seen in decomposition of a double based propellant containing triethyleneglycol dinitrate [137]. For a nitroguanidine propellant, Zhang et al. [138] have reported $\sim$ 10°C decrease in decomposition temperature upon raising nitrogen pressure from 0.1 to 4 MPa. The acceleration of decomposition has been accompanied by a decrease in the activation energy of $\sim$ 50 kJ mol^{-1} that is in part compensated by a decrease in the preexponential factor by $\sim 10^5$ times.

The effect of an inert gas pressure is not limited to reversible or autocatalytic reactions. It can also be remarkable in the case when decomposition of a reactant occurs simultaneously with its evaporation or sublimation. A representative example of such process is decomposition of ammonium perchlorate. Under ambient pressure of flowing nitrogen a DSC curve demonstrates an exothermic peak followed by an endothermic one that respectively represent decomposition and sublimation of this compound [139]. Raising nitrogen pressure to 0.5 MPa suppresses sublimation so that decomposition of ammonium perchlorate shifts to higher temperature and reveals only exothermic events regardless of the crystal size [140]. Since decomposition and evaporation/sublimation generally have different kinetics, changing pressure of an inert gas can be expected to give rise to changes in the overall kinetics of decomposition. In particular, Vargeese [141] reports a decrease in the activation energy of about 20 kJ mol^{-1} for decomposition of ammonium perchlorate when nitrogen pressure is increased from 0.2 to 1.2 MPa.

Just as for ammonium perchlorate, DSC data for decomposition of ammonium dinitramide show an exothermic peak followed by an endothermic one. The process is an overlap of two major channels, one of which produces ammonium nitrate [142]. Under a flow of nitrogen ammonium nitrate decomposes endothermically via dissociative sublimation/evaporation [143] that appears to give rise to the endothermic event in decomposition of ammonium dinitramide. The isoconversional activation energy for this process decreases strongly with conversion approaching the values similar to those found [143] for dissociation of ammonium nitrate [142]. However, under pressure of 5 MPa of nitrogen, evaporation is largely suppressed and the endothermic peak disappears [144]. As a result, the activation energy for the final stages of decomposition of ammonium dinitramide rises by about 20 kJ mol^{-1}.

For waxes, both decomposition and evaporation are endothermic. By analysing two different types of waxes, Muravyev et al. [145] have demonstrated that increasing nitrogen pressure from 0.1 to 1 MPa shifts the overall process to higher temperature and gives rise to a more endothermic value of the process enthalpy. The activation energy of the process under the elevated pressure have been determined to be markedly larger than the activation energy of evaporation.

In conclusion, it should be noticed that there may be cases when increasing an inert gas pressure has no significant effect on the kinetics of decomposition. By way of example, we should mention decomposition of 1,3,5-trinitro-1,3,5-triazine (RDX). The kinetics of this process under nitrogen pressures 0.1 and 5 MPa is described by the Arrhenius parameters that are practically the same for both pressures [144].

5. Conclusions

According to our literature survey, there are three major approaches to exerting pressure on the reactions of thermal decomposition: by manipulating pressure of the product gas, by controlling pressure of an inert gas, and by applying a mechanical force. The latter approach is implemented in diamond anvil cells that permit accomplishing pressure in the GPa range. The decomposition kinetics studies in anvil cells are rare although they are of important value for understanding such phenomena as detonation. At the GPa pressures the acceleration or deceleration of the reaction depends largely on the sign of the activation volume change.

The first two approaches, i.e. manipulating the product and inert gas pressures, are used most commonly. They are implemented routinely in the techniques of thermogravimetric analysis and differential scanning calorimetry that are used widely in studying the kinetics of thermal decomposition. The effect of the product gas pressure on the kinetics of reversible decomposition is rather straightforward. There is a number of models that describe this effect adequately. It has been demonstrated that such models can be used to understand variations in the experimental activation energy as a function of conversion, temperature, and pressure.

The effect of an inert gas pressure on the decomposition kinetics is indirect. An inert gas creates a barrier that slows down the escape of the product gases from the reaction zone. This raises the probability of engaging a product gas in a reaction with either reactant or another product. The probability increases with increasing an inert gas pressure and decreasing the rate of diffusion of the product gas in an inert gas. As a result, reversible and autocatalytic reactions tend respectively to decelerate and accelerate with increasing pressure and/or molecular weight of an inert gas. Unfortunately, there are no established models to describe such effects of an inert gas adequately. Developing such models is most welcome.

Analysis of the literature suggests that the pressure effects on the decomposition kinetics are commonly revealed via changes in the activation energy. This is likely a reason why many publications do not report the values of the preexponential factor. Then again, as discussed here, changes in the activation energy are typically accompanied by changes in the preexponential factor. More importantly, some kinetic effects, such as that of an inert gas pressure, can reveal themselves as changes in the preexponential factor alone. Therefore, more complete kinetic analysis and reporting of its results are highly desired for better understanding of the pressure effects.

Disclosure statement

No potential conflict of interest was reported by the author.

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