

Dispersive kinetics of solid thermolysis. Decomposition of basic aluminium ammonium sulphate¹

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Abstract

The formalism of dispersive kinetics is applied for thermolysis of solids. As an example, the isothermal decomposition of basic aluminium ammonium sulphate in vacuum is analysed. The first order dispersive kinetic equation provides a highly accurate description of thermolysis processes for the three stages of decomposition: partial dehydration at temperatures below 623 K, final dehydration and removal of ammonium in the temperature range 623–873 K, and desulphurisation at temperatures above 873 K.

Keywords: Basic aluminium ammonium sulphate; Kinetics; Stochastic model; Thermolysis

1. Introduction

Classical chemical kinetics was formulated for isolated reactions in homogeneous, three-dimensional, systems [1]. It fails in solids [2–6]. As an example, the classical first order kinetic equation has the form

$$-dc/dt = kc \quad (1)$$

where c is the concentration of the substrate, t is reaction time, and k is specific reaction rate (rate constant). To be applied for thermolysis, Eq. (1) is modified to

$$d\delta/dt = kf(\delta) \quad (2)$$

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¹ Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

where $f(\delta)$ is the proper function for a given reaction model [7–9] for the decomposition fraction

$$\delta = 1 - c/c_0 \quad (3)$$

Formally the use of Eq. (2) is equivalent to a change of reaction order. In common practice, in that way one recovers the constant specific reaction rate or rate constant of classical kinetics and tries to describe its temperature-dependence by the Arrhenius equation

$$k = A \exp(-E/RT) \quad (4)$$

where A is the preexponential factor, E is the activation energy, R is the universal gas constant, and T is the temperature.

From the variety of kinetic model functions $f(\delta)$, one can usually choose the proper one [10] to fit a given set of experimental data but sometimes one finds it necessary to use more than one function for the same system differing only in crystallite sizes or amount of defects. The numerical values of rate constants are, of course, model-dependent.

Furthermore, deviations from the Arrhenius equation are quite common, most probably due to the difference between the idealised process assumed in formulating the kinetic model function and the actual process in the investigated system. To account for these deviations the kinetic model function may be multiplied by some empirical function accommodating the distortion of the actual process from the idealised model [11, 12]. The disadvantage of such an approach is in the use of an empirical accommodation function the physical basis of which is difficult to formulate.

In this paper we present an alternative approach using the first order kinetic equation with the specific reaction rate depending on time, $k(t)$, viz.

$$-dc/dt = k(t)c \quad (5)$$

The starting point of such a formulation of kinetics is that at the molecular level all condensed phase systems are more or less disordered. Thermolysis, by increasing the number of system components, increases the disorder in the system.

The intrinsic property of kinetics [5], as well as transport and relaxation [13], in disordered systems is the time scale invariance: there is no one characteristic time scale, the processes proceed on all experimentally accessible time scales. This phenomenon is accounted for by the use of fractal time, t^α , with $0 < \alpha < 1$. Fractal time is introduced into the kinetic equations by means of a time-dependent specific reaction rate of the form

$$k(t) = (\alpha/\zeta)(t/\zeta)^{\alpha-1} \quad (6)$$

Using this form of time-dependent specific reaction rate one gets from Eq. (5)

$$\delta = 1 - \exp[-(t/\zeta)^\alpha] \quad (7)$$

It seems interesting to note the universal form of Eq. (7). For $\alpha = 1$ Eq. (7) corresponds to the textbook form of the kinetic equation for the first-order reaction, for $1 < \alpha < 4$ to the Avrami equation [14–16] used to describe the sigmoidal δ vs. time

curves for reaction in solids. In physics, $\exp[-(t/\zeta)^\alpha]$ for $0 < \alpha < 1$ is often referred to as the Kohlrausch relaxation function to acknowledge its first use in 1847 by Rudolf Kohlrausch [17] to describe the decay of a residual charge in Leyden jars and its subsequent use by his son Friedrich [18] in his studies of torque relaxation in glass filaments. For $\alpha > 1$, Eq. (7) is also known as the Weibull [19] distribution function in statistical reliability distribution theory. For the kind of distribution function given by Eq. (7), the moments of lifetime distribution are given by

$$\langle (t/\zeta)^n \rangle = \Gamma(1 + n/\alpha) \quad (8)$$

where Γ denotes the Gamma function. For $\alpha = 1$ these moments are reduced to those for monoexponential decay

$$\langle (t/\zeta)^n \rangle = n! \quad (9)$$

From a probabilistic point of view, the use of Eq. (7) instead of an exponential function is equivalent to accounting for the distribution of lifetimes of reactive species in a manner different from that proper for reactions in homogeneous, three-dimensional systems.

For monoexponential decay there is a constant specific reaction rate

$$k = 1/\langle t \rangle \quad (10)$$

cf. Eqs. (6) and (9), and this is the macroscopic parameter which is related to the microscopic rate of single barrier crossing in the familiar pictures of Arrhenius, Eyring or Kramers for thermally activated transitions over the barrier, or of Gamov for quantum mechanical transitions under the barrier. For the decay pattern given by Eq. (7) somewhat more sophisticated phenomenological interpretation, given below, is needed.

In kinetics, the form of Eq. (6), once thought to be empirical, is now fully justified, in the most general way by the stochastic theory of reaction kinetics in dynamically disordered systems [20], and can be used in kinetic equations of any order [3]. In the present paper we are interested in the use of $k(t)$, decreasing in time for $\alpha < 1$, to describe the deceleratory δ vs. time curves for thermolysis. As an example the analysis of the experimental data from the thermal decomposition of basic aluminium ammonium sulphate, BAAS, in vacuum is given below. This system, because of industrial importance of BAAS thermolysis in γ - Al_2O_3 production, has been under constant investigation in Plock's laboratory since the early eighties [21]. So far we have analysed the data using Eq. (2) and different forms of $f(\delta)$.

2. Experimental

The kinetic studies of BAAS thermolysis were performed under isothermal conditions in a standard glass vacuum apparatus equipped with a quartz helix weighing element. The elongation of the helix was measured, by means of a cathetometer, with a precision of 5×10^{-3} mm, which enabled the determination of weight loss with precision of about 10^{-7} g for a sample mass of the order of 10^{-2} g.

For investigation of stage I of BAAS decomposition, see next section, samples were dried to constant weight at 378 K prior to measurements at 473, 523, 543, 563, 578, and 598 K. For investigation of stage II of decomposition, samples were dehydrated to constant weight at 623 K prior to measurements at 648, 673, 723, 756, 793, and 816 K. For investigation of stage III of decomposition, samples were decomposed to constant weight at 837 K prior to measurements at 903, 943, 1008, 1093, 1143, and 1208 K. The decomposition fraction was calculated from

$$\delta = \Delta m / \Delta m_{\max} \quad (11)$$

where Δm is the loss of sample weight for a given heating time, and Δm_{\max} is the maximum loss of weight for a given decomposition stage.

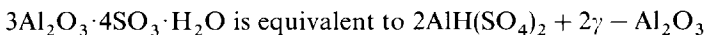
3. Results and discussion

It has been shown [21] that in vacuum, where the process may be considered as practically irreversible, the thermal decomposition of BAAS goes through three stages:

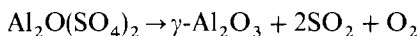
(1) partial dehydration at temperatures below 623 K



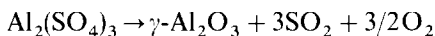
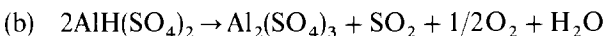
(2) final dehydration and removal of ammonium in the temperature range 623–873 K



(3) desulphurisation at temperatures above 873 K, which proceeds according to two parallel mechanisms:



and



For these stages, Figs. 1–3 present, in the insets, the experimental data in the form of decomposition fraction vs. heating time in min. All these data were found to be adequately fitted by Eq. (7). The solid lines in the insets were drawn using the parameters of the best fits collected in Table 1. From these results, the master curves, δ vs. $(t/\zeta)^\alpha$, were calculated and presented in Figs. 1–3 in the coordinate system δ vs. $(t/\zeta)^\alpha$ on log scale.

There are two reasons for showing the master curves in this coordinate system. The first is to display the goodness of fit, especially at the very beginning of the isothermal decays. The quality of fit is given as the fit standard error, fse in Table 1. For all series of

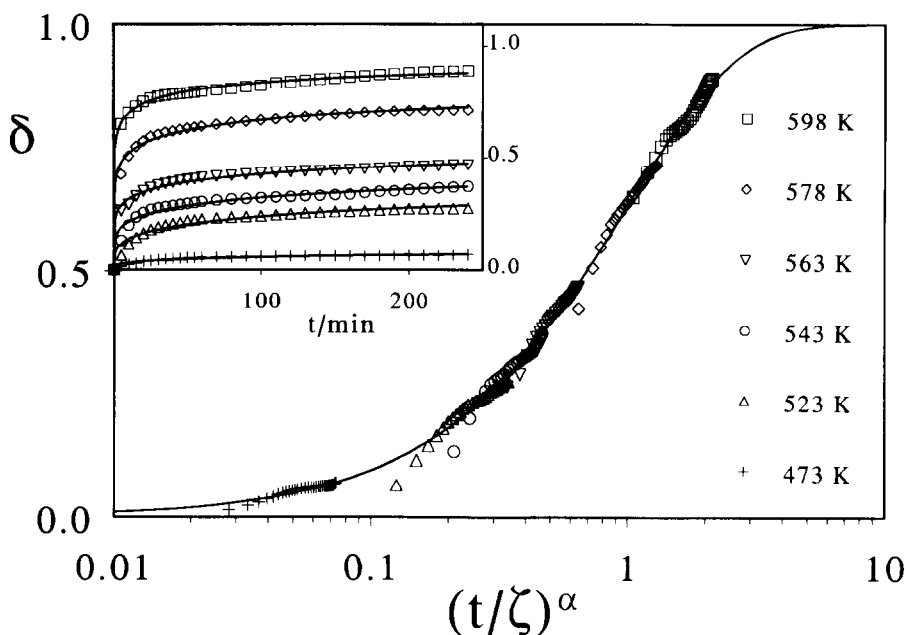


Fig. 1. Kinetics of BAAS decomposition in vacuum, stage I. Inset: experimental data plotted as decomposition fraction δ vs. time of heating at the indicated temperature; solid lines represent the best fit of Eq. (7) for numerical values of timescale, ζ , and dispersion, α , parameters collected in Table 1. Master curve: superimposition of experimental data shown in the inset in coordinate system δ vs. $(t/\zeta)^\alpha$ on a logarithmic scale.

experiments, with the exception of that at 1208 K, as well as for the master curves, f_{se} is of the order of 0.01. Comparable f_{se} values were obtained [21] for the fits using Jander and Ginstling-Brounshtein equations. Both these equations are based on detailed diffusion mechanisms, which provide particular forms of $f(\delta)$ for Eq. (2). Thus the advantage of the present approach is not in a better fit. It is in the sound physical basis of dispersive kinetics and its phenomenological interpretation which is free from the mechanistic details necessary in the classical approach; e.g. the Jander equation is derived under the assumptions of isotropic shrinkage of the spherical substrate grains and parabolic growth of the product layer.

To outline the phenomenological interpretation of Eq. (7) is the second reason of showing the master curves. The decrease of specific reaction rate in time given by Eq. (6) implies that for thermally activated processes, if one takes the familiar Arrhenius picture, the activation energy increases according to

$$E(t) = E_\zeta + (1 - \alpha)RT \ln(t/\zeta) \tag{12}$$

where E_ζ is the activation energy to be estimated from the temperature-dependence of ζ by:

$$E_\zeta = R d \ln \zeta / d(1/T) \tag{13}$$

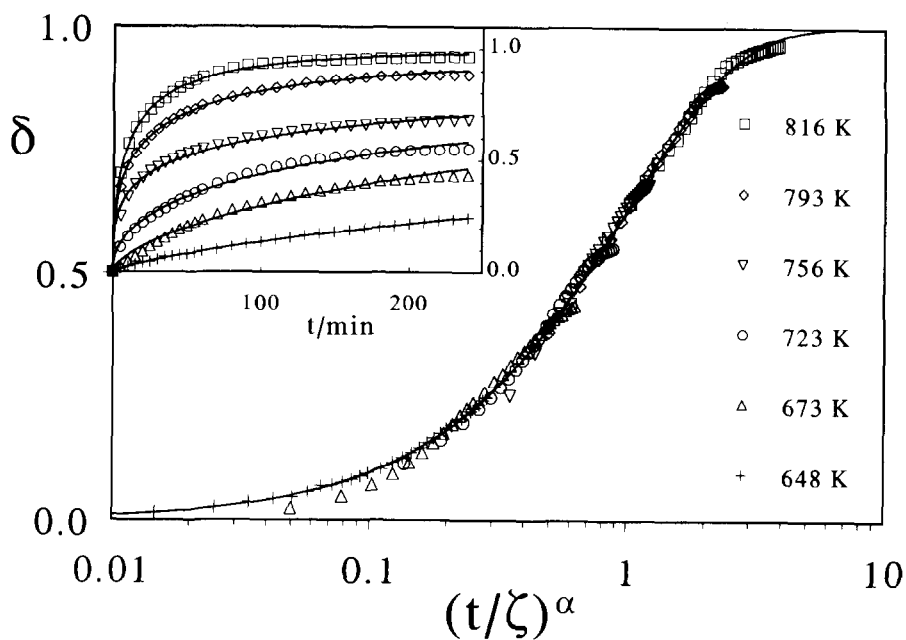


Fig. 2. Same as Fig. 1, for stage II of BAAS decomposition.

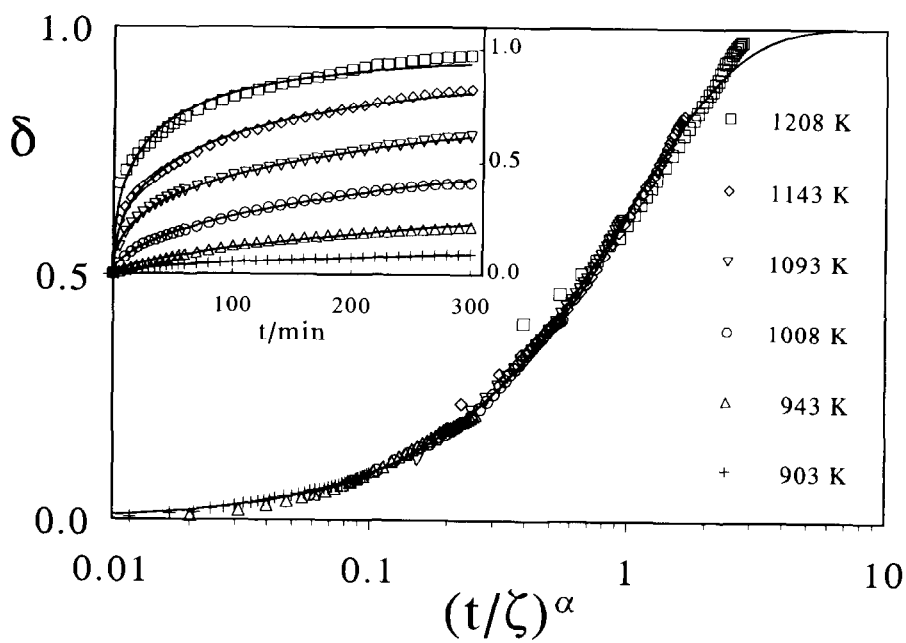


Fig. 3. Same as Fig. 1, for stage III of BAAS decomposition.

Table 1
Timescale, ζ , and dispersion, α , parameters for isothermal decomposition of BAAS in vacuum

Stage	T/K	ζ/min	α	fse^a
I	473	9.52×10^6	0.25	0.004
	523	1.55×10^4	0.26	0.014
	543	1.01×10^4	0.20	0.014
	563	3.43×10^3	0.17	0.009
	578	56.7	0.18	0.013
	598	3.75	0.18	0.008
	648	1.24×10^3	0.77	0.002
II	673	491	0.65	0.016
	723	314	0.48	0.014
	756	134	0.32	0.013
	793	29.0	0.40	0.008
	816	14.4	0.48	0.009
	903	2.44×10^4	0.52	0.002
	943	2.62×10^3	0.62	0.007
III	1008	879	0.55	0.005
	1093	335	0.45	0.005
	1143	107	0.48	0.013
	1208	35.7	0.48	0.027

^a Fit standard error: $fse = \sqrt{\sum_{i=0}^n (\delta_i - \hat{\delta}_i)^2 / (n - p)}$, where: n - number of experimental points, p - number of parameters, δ_i - experimental decomposition fraction, $\hat{\delta}_i$ - calculated decomposition fraction

Taking Eq. (7) as the distribution function of lifetimes, one can write for the distribution of logarithms of lifetimes in units of t/ζ

$$F(\ln(t/\zeta)) = 1 - \exp\{-\exp[\alpha \ln(t/\zeta)]\} \tag{14}$$

and further, cf. Eq. (12),

$$F(u) = 1 - \exp(-\exp u) \tag{15}$$

for the distribution function of activation energy in units of $u = \alpha(E - E_\zeta)/(1 - \alpha)RT$. From Eq. (15), the density of activation energy distribution is given by

$$f(u) = \exp(u - \exp u) \tag{16}$$

Its mean value is equal to

$$\langle u \rangle = -\gamma$$

or

$$\langle E \rangle = E_\zeta - \gamma RT(1 - \alpha)/\alpha \tag{17}$$

where γ is the Euler constant, and the dispersion is given by

$$\sigma_u = \pi/\sqrt{6}$$

or

$$\sigma_E = \pi RT(1 - \alpha)/\alpha\sqrt{6} \quad (18)$$

For $\alpha = 1$ Eqs. (17) and (18) reduce to those proper for classical kinetics, i.e.

$$\langle E \rangle = E_\zeta \quad (19)$$

and

$$\sigma_E = 0$$

Fig. 4 shows the temperature-dependence of E_ζ , cf. Eq. (13), calculated by polynomial interpolation of the numerical values of ζ collected in Table 1. It would be hard to claim that the Arrhenius relationship holds. In the temperature range of the first decomposition stage E_ζ increases from about 130 to about 390 kJ mol⁻¹. The lower value is close to those estimated [21] from the parameters of the Jander equation, 110 and 154 kJ mol⁻¹, and the Ginstling-Brounshtein equation, 93 and 150 kJ mol⁻¹. Comparable increases in the numerical values of E_ζ are seen in the temperature range of the second decomposition stage, from about 20 to about 200 kJ mol⁻¹. For this stage the activation energies estimated [21] from the parameters of the Jander and Ginstling-Brounshtein equations were 82 and 109, and 74 and 96 kJ mol⁻¹, respectively. In

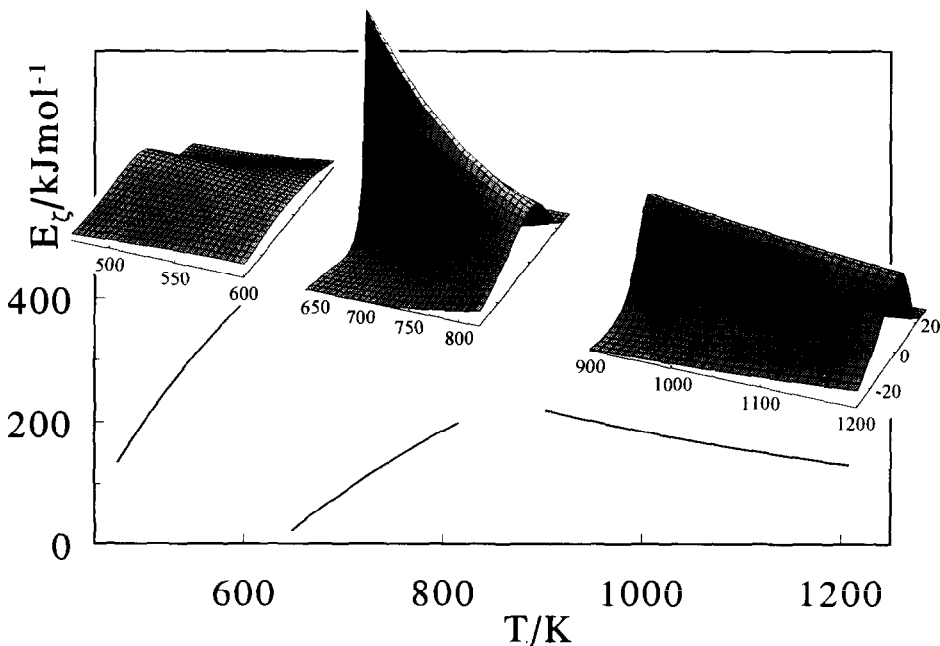


Fig. 4. Temperature-dependence of activation energy E_ζ (solid lines) and of density of activation energy distribution $RTf(E)$ vs. $E - E_\zeta$ (surface plots) for the stages of BAAS thermolysis in vacuum. Further details in text.

contrast with these two stages, in the temperature range of the third decomposition stage E_c decreases from about 220 to 130 kJ mol⁻¹ while the numerical values estimated [21] from the parameters of the Jander and Ginstling-Brounshtein equations are 147 and 128 kJ mol⁻¹. These differences seem to be significant if one ignores the wide distributions of activation energies, exceeding 50 kJ mol⁻¹, displayed in the upper part of Fig. 4. To calculate this distribution, cf. Eq. (16), the numerical values of α , given in Table 1, were approximated, like those of ζ , by polynomial interpolation.

The classical approach insists on single-valued activation energies directly related to the elementary single-barrier processes, admitting, as above, two or at most few distinct processes. Dispersive kinetics allows continuous distributions of activation energies and, in general, a substantial contribution of activation energy for system structural reorganisation to the apparent activation energy for the process followed in the system. This is well evidenced for reactions in the inert solid matrices even in the oversimplified Arrhenius picture [6]. For thermolysis a more sophisticated picture is clearly needed [22]. The fluctuating barrier is a concept whose time appears to have come [23]. The potential barrier to the disassociation of a molecule is seen to depend on the geometric positions of atoms not directly involved what may simply be the stretching of a chemical bond to destruction.

4. Conclusions

Taking into account only the generic property of solids, their disorder at the molecular level, we have reproduced adequately the deceleratory pattern of BAAS thermolysis in vacuum. We have also given a phenomenological interpretation of this reaction pattern free from any mechanistic details. This interpretation differs from that common in the physics of solids [3] in which $1 - \delta$ is represented in the form of a Laplace transform

$$1 - \delta = \int_0^{\infty} g(k) \exp(-kt) dk \quad (20)$$

or

$$\exp[-(t/\zeta)^2] = \int_0^{\infty} f(\tau) \exp(-t/\tau) d\tau \quad (21)$$

for

$$\tau = 1/k \quad (22)$$

and

$$f(\tau) = g(1/\tau)/\tau^2 \quad (23)$$

and $1 - \delta$ is interpreted in terms of superposition of monoexponential decays distributed continuously with the density $f(\tau)$. This latter interpretation is meaningful only for

the rigid-matrix approximation of reaction kinetics in disordered systems, i.e. when the numerical values of α are not increased by matrix dynamic effects [20]. It is, of course, not because the mathematical approach to obtain $f(\tau)$ from relationship (21) fails but because the calculated distributions may have no physical sense. This is also true for the direct use of Eq. (20) to fit the experimental data. There are nearly no restrictions [3] on the form of $g(k)$. One of the most popular forms, tried e.g. for cellulose pyrolysis [24], is that of log-normal distribution of k resulting from assumed Gaussian distribution of activation energies, cf. Eq. (4). This is least surprising, however, as the log-normal distribution mimics the α -stable distribution which as the only one [25] yields Eq. (7) through relationship (21).

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