Available online at www.sciencedirect.com
SCIENCE DIRECT®

Thermochimica Acta 439 (2005) 86–93

thermochimica acta

www.elsevier.com/locate/tca

Experimental test to validate the rate equation "$\mathrm{d}\alpha/\mathrm{d}t = kf(\alpha)$" used in the kinetic analysis of solid state reactions

Michèle Pijolat[*], Françoise Valdivieso, Michel Soustelle

LPMG-CNRS UMR 5124, Centre SPIN, Ecole Nationale Supérieure des Mines de Saint-Etienne, 158 Cours Fauriel,
42023 Saint-Etienne, Cedex 2, France

Received 25 April 2005; received in revised form 23 August 2005; accepted 23 August 2005

Abstract

In order to improve the soundness of the kinetic analysis of solid-state reactions, we present an experimental test based on a sudden change (jump), during an experiment, of the temperature, or of the partial pressure of gases, which have an influence on the kinetic rate. This test, denoted "$f(\alpha)$ test" allows to discriminate if the kinetic modelling may or may not involve the rate equation $\mathrm{d}\alpha/\mathrm{d}t = kf(\alpha)$ for any kind of reaction: thermal decomposition, solids reacting with gases, ... Numerous examples are given and discussed according to the answer of the test, mainly based on the consideration of nucleation and growth processes.

Keywords: Solid state reactions; Kinetics; Rate equation; Nucleation and growth; Rate-limiting step

1. Introduction

In several recent articles, Galwey [1–5] has given a critical description of the literature concerned with the kinetics of solid-state reactions. Since the publications discussing the results of the ICTAC kinetic project [6], he has clearly put in evidence the shortcomings in the mathematical methods generally used for the analysis of the kinetic data, i.e. for the interpretation of the $\alpha(t)$ curves in terms of a "kinetic triplet" E, A_0 and $f(\alpha)$ according to the following rate equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A_0 \exp\left(-\frac{E}{RT}\right) f(\alpha) \qquad (1)$$

E and A_0 being called the "Arrhenius parameters", respectively, the activation energy and the pre-exponential factor; $f(\alpha)$ can take various expressions depending of the model under consideration.

Among the numerous points discussed and criticized in these articles, it appears that the main reasons for claiming that the present situation is "unsatisfactory" [1] come from the great disparity observed in the determination of the Arrhenius parameters by various authors for the same set of kinetic data [6]. What is interesting to notice in all these mathematical methods both for isothermal and non-isothermal data, is that they are based on the assumption that the rate $\mathrm{d}\alpha/\mathrm{d}t$ of a "simple" reaction obeys to the following conditions:

(a) it varies with temperature according to the Arrhenius equation;
(b) α is a separate variable in the expression of the rate (cf. Eq. (1) or an equation of the type $g(\alpha) = kt$).

The term "simple" means in general that the reaction stoichiometry is well established, there are no parallel reactions, no successive reactions, no melting, etc. However, it is worth trying to give a definition of it. A simple reaction is a transformation which satisfies two conditions: (1) There is no intermediate solid phase from the initial to the final solid phases. For example, oxidation of copper by oxygen into CuO with formation of the intermediate phase Cu_2O is not a simple reaction but a succession of two simple reactions, each of them having its own model of transformation with nucleation and growth mechanisms. (2) There does not exist a large departure from stoichiometry in the initial and final phases.

One of the aims of the present article is to show that even in the case of simple reactions, the rate may not fulfil both conditions

---

[*] Corresponding author. Tel.: +33 477 420 152; fax: +33 477 499 694.
E-mail address: mpijolat@emse.fr (M. Pijolat).

0040-6031/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2005.08.038

(a) and (b) so that Eq. (1) is inadequate for the description of the kinetic set of data, whatever the experimental operating procedures could be. First, concerning the variation of the rate with temperature, the Arrhenius dependence must be considered as a very restrictive assumption, for (at least) the following reasons:

- the rate of a rate-limiting elementary step is the result of two kinetic processes, the direct and the reverse one, and unless the reaction is done within experimental conditions (P, T) far from those of equilibrium, the rate of the reverse process cannot be neglected besides the rate of the direct one;
- solid state reactions involve gaseous species that can be adsorbed or/and desorbed; thus, depending of which of the elementary steps is controlling the reaction, the equation giving the amount of adsorbed species in equilibrium with the gaseous phase (very often it is the Langmuir isotherm), will be involved in the rate equation, i.e. $\mathrm{d}\alpha/\mathrm{d}t$ proportional to a term of the type "$AP_j/(1+\sum B_iP_i)$", in which A and B follow Arrhenius dependence with temperature (see for example Ref. [7]);
- intensive variables other than temperature and pressure may also be involved such as for example the activity of constituents in solid solutions.

More generally the rate should thus be expressed as follows:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A(T, P_i, \ldots)\, f(\alpha) \tag{2}$$

in which A has not the meaning of a rate constant, which explains why the letter "k" is not used in this article.

Concerning the proportionality between the rate $\mathrm{d}\alpha/\mathrm{d}t$ and a function $f(\alpha)$, we report in this article a method based on an experimental test to settle the validity of Eq. (2) for any reaction. The principle of this "$f(\alpha)$ test" is given in Section 2, and examples of application to various kinds of solid state reactions are reported in Section 3. In Section 4, we discuss the two situations that occur according to the result of the $f(\alpha)$ test, i.e. for what reasons the rate follows or does not follow Eq. (2). We comment on the shortcomings of the mathematical methods based on the use of Eq. (2), and on the interest of making the $f(\alpha)$ test for choosing an appropriate kinetic model involving nucleation and growth steps.

2. Principle of the "$f(\alpha)$ test"

2.1. Preliminary justification

As mentioned in the introduction part, Eq. (1) is at the basis of most of the kinetic analysis of experimental data. However, despite of many articles devoted to mathematical methods more and more sophisticated and automated in order to interpret rapidly the thermal kinetic data, the assumptions on which are based the various types of $f(\alpha)$ functions generally used to fit the data, are not enough discussed or commented in relation with the geometrical or morphological characteristics of the solid particles [5]. The $f(\alpha)$ functions are usually classified using capital letters with a subscript n, such as A_n, F_n, R_n, D_n, ... and the best fit between one of these functions and the set of kinetic data gives the kinetic "model" and the kinetic parameters E and A. In general, the subscript n is related to the geometrical characteristics of the reacting solid particles.

To account for both nucleation and growth processes, A_n laws (which are well known as Avrami–Erofeev equations), which correspond to sigmoid $\alpha(t)$ curves, have been derived upon the assumption that one of the two processes was predominant on the other one. On the contrary, R_n and D_n laws are used when nucleation is supposed to occur instantaneously at the beginning of the reaction, and thus in this case only growth is involved in the kinetic modelling. In the case of Avrami–Erofeev laws, the nuclei are supposed to appear everywhere in the bulk of the particles, but this situation is not always encountered as for example with many reactions of inorganic compounds (decompositions, solids reacting with gases, ...) where the nuclei are observed to appear at the surface of the particles. In fact, such reactions can be more realistically described using the Mampel's model [8] (or Johnson and Mehl's model [9]) which is based on the combination of geometrical and statistical approaches: the rate limiting step of growth is assumed to occur at the interface between the reactant and the product phases, and the nucleation process follows a Poisson spatial temporal distribution. The calculation of the rate according to Mampel assumptions can be done for plate-like, cylindrical and spherical particles; it involves a couple of kinetic "constants" (γ, ϕ), related to the rates of nucleation and growth, respectively. The constant ϕ is relative to the growth process and it is defined as the amount of reactant transformed per meter square per second (we have called ϕ the "areic reactivity of growth"); for example, if V_m represents the molar volume of the reactant, $V_\mathrm{m}\phi$ is the rate of advance of the interface in the case of the core-shrinking model R_n. The constant γ is defined as the areic frequency of nucleation, it is a number of nuclei per meter square per second. These two kinetic parameters are assumed to vary independently versus temperature, partial pressures of gaseous species, impurities, etc. since the mechanisms of nucleation and growth should be different. In practice, the calculations are greatly facilitated by the use of a dimensionless time variable (θ), which leads to the comparison of $(\mathrm{d}\alpha/\mathrm{d}\theta)/(\mathrm{d}\alpha/\mathrm{d}\theta)_{\alpha=0,5}$ (the calculated reduced rate) to $(\mathrm{d}\alpha/\mathrm{d}t)/(\mathrm{d}\alpha/\mathrm{d}t)_{\alpha=0,5}$ (the experimental reduced rate, for P_i and T constant). The best agreement between experiments and model is found by means of a unique fitting parameter A_M ($A_\mathrm{M} = 4\pi r_0^3\gamma/\phi V_\mathrm{m}$ for spherical particles of initial radius r_0 and molar volume V_m). It is interesting to notice that ϕ and the factor A (in Eq. (2)) are related according to:

$$A = \frac{n\phi V_\mathrm{m}}{r_0} \tag{3}$$

where n is equal to 1, 2, or 3 for plates, cylinders, or spheres, respectively; r_0 is the initial radius of the spheres or cylinders, and the half thickness in case of plates.

It is important to notice that the rate derived from the Mampel's model is not consistent with Eq. (2), as it can be very schematically illustrated in Fig. 1. We have chosen two kinds of nucleation and growth which lead to the same conversion ($\alpha = 0.5$) of a spherical particle: a single nucleus in (a) and two nuclei in (b). Due to Mampel's assumptions, for identical conditions of T, P_i, ... the rate corresponding to the particle in

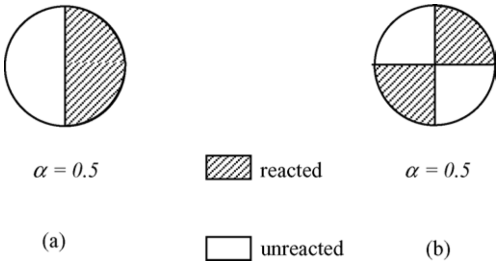

Fig. 1. Schematic representation of particles with same fractional conversion (= 0.5) and distinct rates of transformation in case of one (a) or two nuclei (b).

(b) is twice the rate in (a) since the surface of the advancing interface in (b) is twice that in (a). Since the Mampel's model is able to account for a sigmoid shape of $\alpha(t)$ curves, it was possible to interpret our kinetic data in several cases, like for example Ce(OH)CO_3 [10] and $CaCO_3$ [11] decompositions. As it will be reported below (Section 4.2), in case of nucleation at the surface of the solid, not only Mampel's model but other nucleation—growth models can be proposed that give a rate which is not in agreement with Eq. (2), i.e. a rate without a "$f(\alpha)$" behaviour.

So, considering nucleation-growth reactions may occur with surface nucleation (and thus without a "$f(\alpha)$" behaviour) or with volume nucleation (with a "$f(\alpha)$" behaviour), it has seemed to us primordial to be able to choose between both alternatives, since it is most often very difficult or quite impossible to unambiguously decide it from microscopic observations. More generally, it is important to know if α a separable variable of the rate, or not, for any kind of solid-state reaction. We thus propose an experimental test, called the "$f(\alpha)$" test, which does not rely on any assumption concerning the mechanism or the kinetic model. This test is valid even if the rate does not follow the Arrhenius law (cf. Eq. (2)).

2.2. *The description of the "$f(\alpha)$ test"*

The test is based on two experiments conducted as follows:

- during the first experiment, the temperature (T) and the partial pressures of all the gases (P_i) reacting with or produced by the solid are maintained constant up to $\alpha \approx 1$;
- the second experiment is done with a different temperature T' (or pressure P_i') up to a value of α between ~0.2 and ~0.7, then a sudden change is done to return to the same conditions T and P_i as in the first experiment.

Fig. 2 shows the two kinds of results that can be observed by plotting dα/dt versus α for both experiments: in (a) the curves of the rate are superimposed which means that a $f(\alpha)$ function can be used for the choice of the kinetic model; in (b), since the rates are found to be different for the same value of α, and A is unchanged (T and P_i are rigorously identical), α is not a separate variable of the rate and Eq. (2) is not valid. The interest of this method is that it does not require any mathematical analysis of the experimental data. In the next section, we present the results of the "$f(\alpha)$ test" for several reactions studied in our laboratory during these last years.

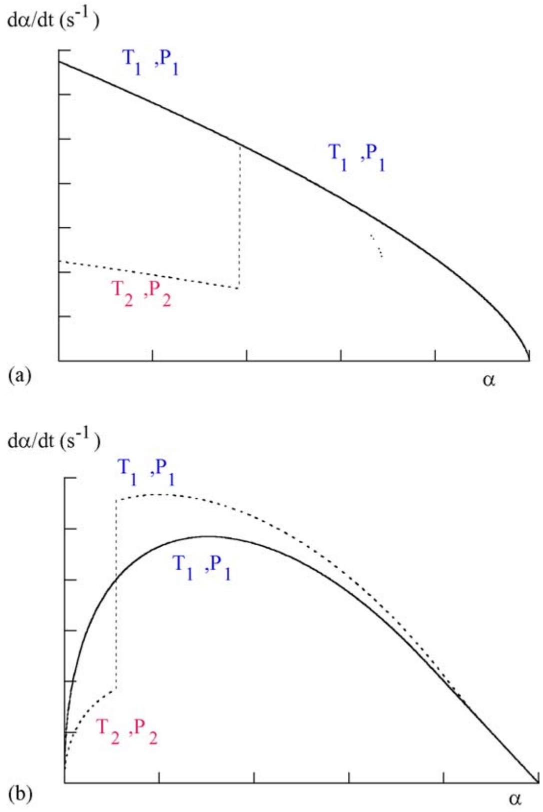

Fig. 2. Illustration of the "$f(\alpha)$" test with an isothermal and isobaric experiment (continuous line) and a temperature jump from T_2 to T_1 (dotted line): α is a separate variable of dα/dt in (a) whereas it is not in (b).

3. Application of the "$f(\alpha)$ test" to several solid state reactions

Various kinds of solid-state transformations have been studied using Eq. (2) for the analysis of the experimental kinetic data. Here, we give the results of the "$f(\alpha)$ test" in three cases: decomposition (including dehydration), reactions between gases and solids, and reactions between two solids. It is worthwhile to mention that all the experiments were done with a very small mass of sample in the crucible of a thermobalance (~25 mg) in order to avoid the issue of mass and heat transfer in the powder bed, and thus to ensure as far as possible isothermal and isobaric conditions during all the reaction.

3.1. *Decomposition, dehydration, dehydroxylation*

$CaCO_3$ decomposition has been very extensively studied under various experimental conditions, and there is still a debate on the precise mechanism and on the elementary step controlling the growth. Isothermal and isobaric $\alpha(t)$ curves exhibit a sigmoid shape, indicating a continuous nucleation process. The literature data concerning the values of $\ln A_0$ and E are remarkably widespread [13–14].

Fig. 3 shows the result of the "$f(\alpha)$ test", the conditions used for the two experiments are given in the legend (as for the other examples reported hereafter). It can be seen that the two curves after the pressure jump are not superimposed, and thus the con-

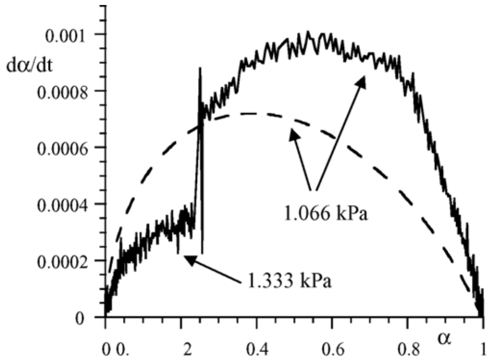

Fig. 3. "$f(\alpha)$" test in the case of the decomposition of $CaCO_3$: jump in CO_2 pressure from 1.333 to 1.066 kPa (the temperature was fixed to 700 °C).

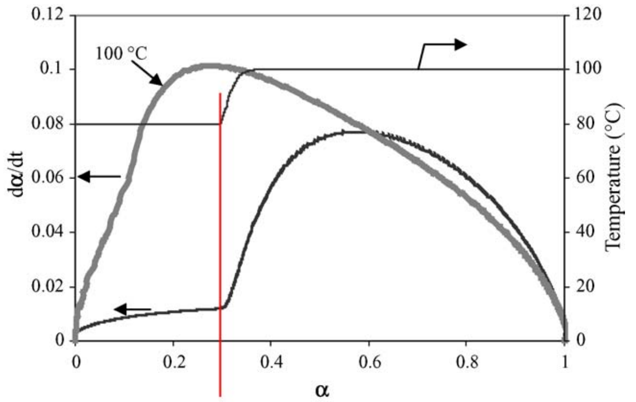

Fig. 4. "$f(\alpha)$" test in the case of the dehydration of Li_2SO_4, H_2O: jump in temperature from 80 to 100 °C (the water vapour pressure was fixed to 0.26 kPa).

sequence is that the kinetic curves cannot be analysed using the assumption of a $f(\alpha)$ function as in Eq. (1) or (2).

In Fig. 4, we have reported the plot of $d\alpha/dt$ curves versus α obtained for the "$f(\alpha)$ test" method applied to the dehydration of Li_2SO_4, H_2O. Again the lack of agreement between the two curves after the sudden change indicate that the use of a $f(\alpha)$ function in the rate equation must be avoided.

Similar conclusions could be drawn from the results obtained for the dehydroxylation of kaolinite into metakaolinite (Fig. 5). The interpretation of the shape of the experimental curves of $d\alpha/dt$ versus α could be done for each of these reactions by means of nucleation—growth models as previously detailed elsewhere [10–11,15,16].

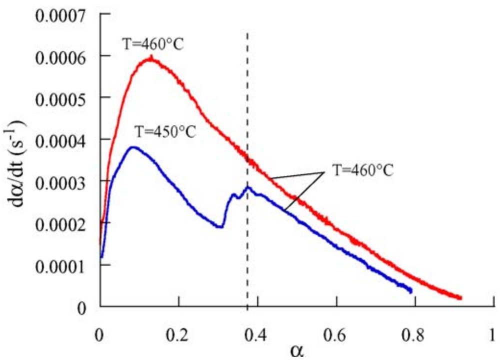

Fig. 5. "$f(\alpha)$" test in the case of the dehydration of kaolinite ($Si_2Al_2O_9(OH)_4$): jump in temperature from 450 to 460 °C (the water vapour pressure was fixed to 0.25 kPa).

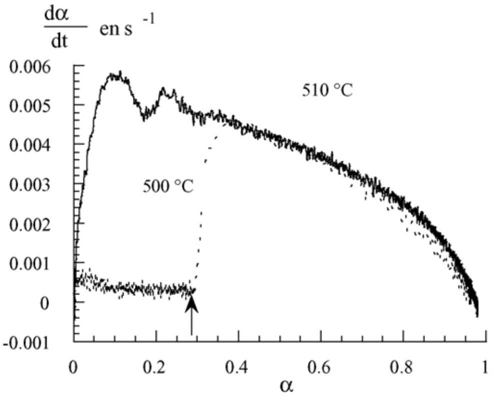

Fig. 6. "$f(\alpha)$" test in the case of the oxidation of magnesium particles: jump in temperature from 500 to 510 °C (the oxygen pressure was fixed to 20 kPa).

These examples show that obviously the kinetic analysis methods based on Eq. (1) would lead to values of A_0 and E with no real meaning, which is the case of mathematical fitting with an erroneous law.

3.2. Reactions between gas and solids

Since several years, we have been interested (mostly for research supported by industry) in two kinds of gas–solid reactions: oxidation of metals and alloys, and reduction of oxides. We present, hereafter, the results of the "$f(\alpha)$ test" performed during studies on Mg/O_2, Zr/O_2, U_3O_8/H_2 and U_3O_8/NH_3 systems.

The oxidation of magnesium particles (Fig. 6) exhibits a remarkably "$f(\alpha)$" behaviour of the rate since the curves of $d\alpha/dt$ after the sudden change in T or P are very well superimposed [17]. The same behaviour (Fig. 7) was observed in the reaction of oxidation of zirconium in the alloy Zy4 well known as zircaloy in nuclear energy production [18]. It can be seen in Fig. 7 that after each jump of temperature from 500 to 530 °C, all the rate curves (dm/dt plotted versus m%, where m is the weight change) are very well superimposed after the jumps. An explanation to this "$f(\alpha)$" behaviour in the case of these two reactions is that

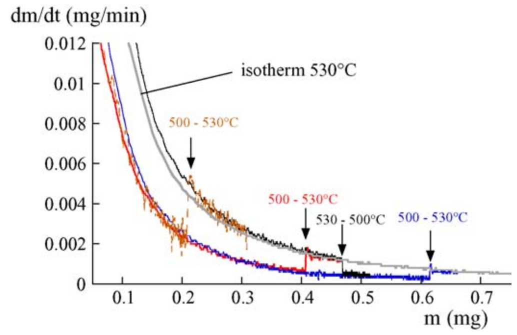

Fig. 7. "$f(\alpha)$" test in the case of the oxidation of zircaloy by water vapour: jumps in temperature from 500 to 530 °C or inversely as indicated by the arrows (the partial pressures in water vapour and hydrogen were fixed to 1.3 and 1 kPa, respectively).

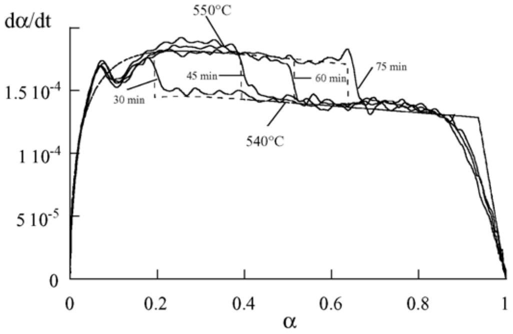

Fig. 8. "$f(\alpha)$" test in the case of the reduction of U_3O_8 by hydrogen into UO_2: jumps in temperature from 550 to 540 °C (the partial pressures in hydrogen and water vapour were fixed to 2.0 and 0.6 kPa, respectively).

metal surfaces are always covered with a very thin film of oxide, so only the growth process is at the origin of the variations of α with time of oxidation (the nucleation process does not take part to the reaction).

We have also studied the transformation of uranium oxide powders from U_3O_8 into UO_2 using reducing gases such as H_2 or NH_3. The system U–O is known to exhibit a very complex chemistry with various intermediate non-stoichiometric oxides. In the case of the reduction of U_3O_8 by hydrogen, after a previous erroneous kinetic analysis [19], we have reinterpreted the kinetic data (isothermal, and isobaric curves which means that the partial pressures in hydrogen and water vapour were maintained constant during the course of the transformation) to take into account three successive simple reactions: $U_3O_8 \rightarrow U_3O_{8-x} \rightarrow U_4O_9 \rightarrow UO_2$ [20]. The "$f(\alpha)$ test" applied to this transformation was found to be validated in each of the three reactions as shown in Fig. 8. In the case of the reduction of U_3O_8 into UO_2 by ammonia (there the partial pressures in NH_3, H_2O and N_2 were fixed during all the experiments) we observed only two steps: $U_3O_8 \rightarrow U_3O_{8-x} \rightarrow UO_2$ (no U_4O_9 phase could be detected in the X-ray diffraction patterns). The variations of dα/dt versus α have a sigmoid shape (which was not the case for those obtained with hydrogen as the reducing gas). The "$f(\alpha)$ test" shown in Fig. 9 indicates that the rate does not vary as expressed by Eq. (1) or (2).

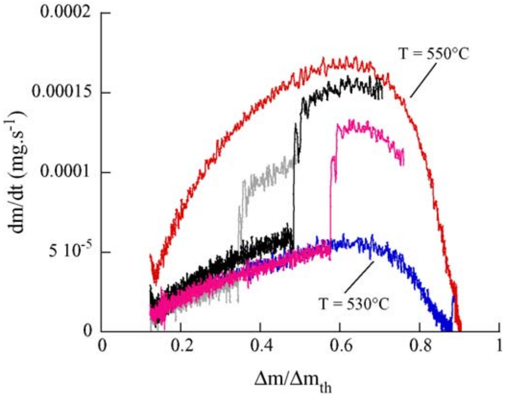

Fig. 9. "$f(\alpha)$" test in the case of the reduction of U_3O_8 by ammonia into UO_2: jumps in temperature from 530 to 550 °C (the partial pressures in ammonia, nitrogen and water vapour were fixed to 0.625, 0.275 and 0.85 kPa, respectively).

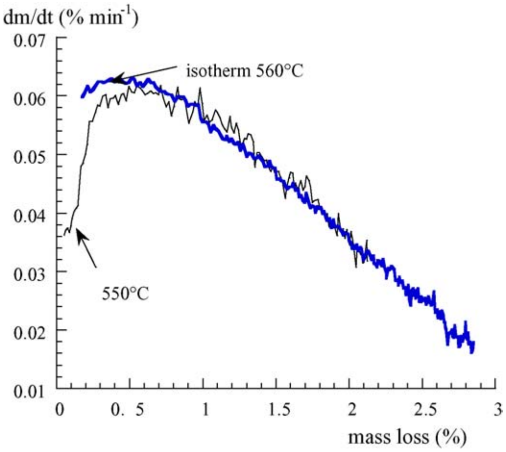

Fig. 10. "$f(\alpha)$" test in the case of the reduction of U_3O_8 by carbon intoUO_2: jump in temperature from 550 to 560 °C (the partial pressures in CO_2 was fixed to 5.0 kPa).

3.3. Reactions between solids

The synthesis of UO_2 powders may also be achieved by the reduction of U_3O_8 by carbon; in this case a mixture of U_3O_8 and C powders is heated in a gaseous flow containing a fixed partial pressure in CO_2 since CO_2 was observed to be the only gas produced by the reaction. Fig. 10 shows that the "$f(\alpha)$ test" is validated.

4. Comments and conclusions

The application of the "$f(\alpha)$ test" to various kinds of solid state reactions leads to a possible classification in two families, according to the answer "yes" or "no" to the question: is α a separate variable of dα/dt? Various situations may be distinguished within each of both families as commented below.

4.1. α is a separate variable of dα/dt

When the "$f(\alpha)$ test" is successful, it means that an expression for $f(\alpha)$ can be found among the "kinetic models" A_n, R_n, D_n,[1] etc. of the literature, that fits correctly the kinetic data obtained in isothermal and isobaric conditions, taking into account the geometrical shape of the initial particles, and if necessary a particle size distribution. It is only when the rate follows the Arrhenius equation that non-isothermal data could be also correctly interpreted, otherwise whatever the mathematical method could be, it would lead to E values varying with α (or T). In most cases,

---

[1] D_3 and D_4 laws are proposed in the case of growth controlled by a diffusion step in the product layer. The D_3 law (or Jander's law) for spherical particles results from the combination of the equation of the contracting volume R_3 with the parabolic law of diffusion (established for plates), and has no really physical meaning. Only D_4 law should be used in case of spherical particles (Ginstling and Brounstein's law) or a modification of D_4 law when the ratio of the molar volumes of the reactant and the product is different from 1 (Valensi–Carter's law). We think that D_3 law should disappear from the tables in the articles relative to kinetic analysis, as well as from the software joined to the commercial devices of thermal analysis.

Table 1
Various assumptions useful in kinetic models for solid state transformations and related answer to the $f(\alpha)$ test

		Rate limiting step of growth	Shape of the particles		
			Spheres	Cylinders	Plates
Instantaneous growth continuous nucleation $f(\alpha)$ test ⇒ yes		–	F_1	F_1	F_1
Instantaneous nucleation $f(\alpha)$ test ⇒ yes	Inward development	Internal interface	R_3	R_2	R_1
		External interface	(a)	(a)	(a)
		Diffusion	D_4	D_2	D_1
	Outward development	Internal interface	(a)	(a)	(a)
		External interface	(a)	(a)	(a)
		Diffusion	(a)	(a)	(a)
Surface nucleation-anisotropic growth $f(\alpha)$ test ⇒ no	Inward development	Internal interface	(a)	(a)	(a)
		External interface	(a)	(a)	(a)
		Diffusion	(a)	(a)	(a)
	Outward diffusion	Internal interface	(a)	(a)	(a)
		External interface	(a)	(a)	(a)
		Diffusion	(a)	(a)	(a)
Surface nucleation-isotropic growth $f(\alpha)$ test ⇒ no	Inward development	Internal interface	Mampel	Mampel	Mampel
		External interface	(b)	(b)	(b)
	Outward development	Internal interface	(c)	(c)	(c)
		External interface	(c)	(c)	(c)
Bulk nucleation-isotropic growth $f(\alpha)$ test ⇒ yes		Internal interface	A_3	A_2	A_1

(a): calculated for $Z=1$ and $Z\neq 1$ in CIN2[2]; (b): calculated for $Z=1$; (c): not yet calculated.

this can be at the origin of many of the shortcomings outlined and largely discussed in Ref. [1–5].

Moreover, it appears also that the mathematical methods based on isothermal kinetic data appear well adapted for finding the expression of $f(\alpha)$ provided the experiments are done in isobaric conditions with respect to all the gases participating to the reaction. In such cases, it is interesting to mention that the variations of ϕ versus temperature and partial pressure P_i can be obtained from the kinetic analysis of the experimental data acquired in various settled conditions (T, P_i).

An other possible situation is that of a reaction for which the "$f(\alpha)$ test" is valid but none of the $f(\alpha)$ functions of the literature appears to satisfactorily fit the isothermal kinetic data. This may happen in (at least) two situations:

- The "kinetic model" (i.e. the expression of $f(\alpha)$) has not yet been established or reported in the literature. It could be, for example, the case of particles with inward growth controlled by an elementary step located at the external interface like for example an adsorption or desorption step, or a reaction between adsorbed species. So it has been possible to establish expressions of $f(\alpha)$ different from the usual R_n or D_n ones, taking into account also the possible change in the molar volume between the reactant and product phases. In the table, we have reported the various assumptions from which the mathematical expressions of $f(\alpha)$ can be derived.[2]
- The transformation under study is not simple and results from consecutive or parallel reactions. This last situation has already been discussed in the case of simulated kinetic data of the ICTAC project [6]. The formation of intermediate phases during the transformation of a reactant A into a product B is not always easy to detect (amorphous phase, melting phase, ...) but it is a quite frequent situation, as for the reduction of uranium oxide by hydrogen (cf. Section 3.2). When three consecutive reactions happen, each of them will proceed according to their own rate equation, i.e. a particular couple of ϕ and $f(\alpha)$ functions. In the example illustrated in Fig. 8, the "$f(\alpha)$ test" is verified in each domain of the extent of conversion α, which is in fact an "apparent α" resulting from the combination of three "real" degrees of conversion defined with respect to the three successive reactions [20].

4.2. *α is not a separate variable of $d\alpha/dt$*

As previously discussed in Section 2, this situation may correspond to the reactions involving continuous nucleation and growth, when the nucleation process occurs at the solid surface. The (simple) reactions for which the nucleation and growth process occur according to the assumptions of the Avrami–Erofeev equation would verify the "$f(\alpha)$ test". In all other cases, two kinds of models can be used to interpret the variations of the rate with time or with α (cf. Table 1):

---

[2] In our laboratory, we are using a software tool "CIN2" for several years in which the various assumptions listed in the table can be selected before calculating α and $d\alpha/dt$ variations. It allows the calculation of nucleation-growth models (Mampel, anisotropic growth) for plates, cylinders and spheres. More recently, Monte-Carlo simulations for nucleation-growth models in case of cubes have been developed [26].

- The Mampel's model, which relies on the assumptions of *isotropic* growth of the nuclei and a rate-controlling step of growth located at the internal interface (cf. Section 2.1).
- A model of nucleation at the surface of the particles followed by *anisotropic* growth: in this case the lateral growth (i.e. tangentially to the surface of the particles) is supposed to be "quasi" instantaneous compared to the radial growth; the calculation of α and $d\alpha/dt$ can be done in a similar manner than in the Mampel's model (i.e. using a dimensionless time θ and a parameter A_M) for plates, cylinders and spheres, assuming either inward or outward development, and that the rate-limiting step of growth could be an interface step (external or internal interface) or a diffusion step. For example, we reported in a previous article that the kinetic curves obtained for the dehydration of a powder of Li_2SO_4, H_2O in isothermal and isobaric conditions, could be accounted by the model of nucleation and anisotropic growth controlled by an elementary step located at the internal interface [15].

As in Section 4.1, it must be mentioned that in the case of parallel or consecutive reactions, none of these models could obviously account for the variations of the rate versus time. The problem of complex reactions is that it is sometimes rather difficult to ascertain the presence of intermediate phases, even by coupling different techniques (microscopy, spectroscopy, X-ray diffraction, ...). It has been proposed to use mathematical methods like isoconversion free-model ones [21–22] and to see if E varies with α or with temperature. However, we have already seen that this may occur even for "simple" reactions, when for example the Arrhenius law is not followed (cf. Section 4.1). So, we have designed an other experimental test, without any theoretical assumptions, based again on the experiments of sudden change (jumps in temperature or pressure), in order to put in evidence in what ranges of α the reaction could be accounted by a simple reaction. We intend to describe this test, its advantages, and to give examples of illustration in a future article.

In addition, it must be recalled that the assumption of a rate-limiting elementary step of growth necessarily induces that the reacting system progresses in conditions of steady state. Galwey and Brown have already mentioned [23] that "ideally, both isothermal DSC and DTG results, recorded under similar conditions, should be compared to confirm the kinetic behaviour". Experimentally it was already done in our laboratory by Lalauze et al. [24] using separate TG and microcalorimeter apparatus connected with the same gaseous atmosphere. At present this can be done very simply using commercial thermobalances equipped with heat flow meters (a DSC device used in isothermal and isobaric conditions). It has led us to settle another experimental test for the verification of the steady-state approximation. Moreover, it can also be very useful to detect consecutive reactions (as in the case of the reduction of U_3O_8 by hydrogen), since the scale factor between dQ/dt (heat flow) and dm/dt (mass gain rate) must be straight related to the enthalpy of reaction [18,25].

Finally, an advantage of the models of nucleation-growth (surface nucleation and either isotropic or anisotropic growth) presented above, is that the values of the kinetic "constants" γ and ϕ, related to respectively the nucleation and the growth can be obtained from the confrontation of the measured rate to the calculated rate for each set of T, P_i conditions prevailing during the isothermal isobaric experiments. So in general, from the determination of the kinetic model we can get the variations of $\gamma(T, P_i)$ and $\phi(T, P_i)$, propose corresponding mechanisms, i.e. sets of elementary steps, then calculate the possible laws for γ and ϕ assuming that one of these steps is rate-limiting [16–20]. Moreover, we have also shown in various studies how the variations $\phi(T, P_i)$ can be obtained directly from experiments and without any assumption, using (again) the sudden change method [10,12,16–19,25]. It will also be interesting to detail the basis and the advantages of this method in future articles.

As a concluding remark, we hope that this attempt to investigate solid state transformations using experimental tests in order to choose the appropriate kinetic assumptions and the appropriate kinetic model will contribute to overcoming some of the difficulties frequently encountered in this research field.

Acknowledgement

We thank Loïc Favergeon, doctorate student in the laboratory for the experiments performed on lithium sulphate dehydration (Fig. 4).

References

[1] A.K. Galwey, Thermochim. Acta 413 (2004) 139.
[2] A.K. Galwey, Thermochim. Acta 399 (2003) 1.
[3] A.K. Galwey, Thermochim. Acta 397 (2003) 249.
[4] M.E. Brown, A.K. Galwey, Thermochim. Acta 387 (2002) 173.
[5] A.K. Galwey, M.E. Brown, Thermochim. Acta 386 (2002) 91.
[6] M.E. Brown, M. Maciejewski, S. Vyazovkin, R. Nomen, J. Sempere, A. Burnham, J. Opfermann, R. Strey, H.L. Anderson, A. Kemmler, R. Keuleers, J. Janssens, H.O. Dsseyn, Chas-Rui Li, B. Tong, B. Tang, J. Roduit, T. Malek, Mitsuhashi, Thermochim. Acta 355 (2000) 125.
[7] J.M. Criado, F. Gonzales, M. Gonzales, Thermochim. Acta 24 (1982) 59.
[8] K.L. Mampel, Z. Phys. Chem. A 187 (1940) 235.
[9] W.A. Johnson, R.F. Mehl, Trans. Am. Inst. Min. Met. Eng. 135 (1939) 416.
[10] J.P. Viricelle, M. Pijolat, M. Soustelle, J. Chem. Soc. Faraday Trans. 91 (1995) 4431.
[11] V. Bouineau, M. Pijolat, M. Soustelle, J. Eur. Ceram. Soc. 18 (1998) 1319.
[12] M. Soustelle, M. Pijolat, Solid State Ionics 95 (1997) 33.
[13] A.K. Galwey, M.E. Brown, Thermochim. Acta 300 (1997) 107.
[14] M.E. Brown, J. Therm. Anal. 49 (1997) 17.
[15] F. Valdivieso, V. Bouineau, M. Pijolat, M. Soustelle, Solid State Ionics 101–103 (1997) 1299.
[16] K. Nahdi, S. Perrin, M. Pijolat, F. Rouquerol, N. Ariguib, M. Ayadi, Phys. Chem. Chem. Phys. 4 (2002) 1972.
[17] K. Surla, F. Valdivieso, M. Pijolat, M. Soustelle, M. Prin-Lamaze, Annales de Chimie, Science des Matériaux 25 (2000) 601.
[18] M. Tupin, M. Pijolat, F. Valdivieso, M. Soustelle, A. Frichetand, P. Barberis, J. Nucl. Mater. 317 (2003) 130.

[19] C. Brun, F. Valdivieso, M. Pijolat, M. Soustelle, Phys. Chem. Chem. Phys. 1 (1999) 471.
[20] S. Perrin, M. Pijolat, F. Valdivieso, M. Soustelle, Electrochem. Soc. Series 16 (2003) 477.
[21] S. Vyazovkin, Thermochim. Acta 355 (2000) 155.
[22] S. Vyazovkin, Thermochim. Acta 397 (2003) 269.
[23] A.K. Galwey, M.E. Brown, Thermochim. Acta 269/270 (1995) 1.
[24] R. Lalauze, A. Souchon, M. Soustelle, Oxidat. Met. 10 (1976) 105.
[25] S. Perrin, Doctorate Thesis, Saint-Etienne, France, 2002.
[26] C. Helbert, E. Touboul, S. Perrin, L. Carraro, M. Pijolat, Chem. Eng. Sci. 59 (2004) 1393.