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Experimental tests to validate the rate-limiting step assumption used in the kinetic analysis of solid-state reactions

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ABSTRACT

The kinetic analysis of experimental data obtained in the case of solid-state reactions (thermal decompositions, reactions of gases with solids) relies on various assumptions among which two are of very high importance: the steady-state approximation and the rate-limiting step. Both assumptions may be verified using simple experimental tests. The first one needs the coupling of measurements of the kinetic rate by two methods (in general thermogravimetry and calorimetry). The second one is based on sudden changes (jumps), during an experiment, of the temperature, or of the partial pressure of gases which have an influence on the kinetic rate. The basic principles of these tests are first explained, then various examples are given in order to illustrate their application to solid-state reactions.

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1. Introduction

Several recent articles have pointed out the difficulty of the kinetic analysis of experimental data for elucidating the mechanism of solid-state reactions, such as decomposition and reactions of solids with gases [1–3]. Among the reasons that can be involved in front of the deficiencies of the usual theories and concepts, it is really important to consider:

(1) the necessity of precise information on the chemical nature of the transformation,
(2) the necessity of measuring the kinetic rate in controlled temperature and pressure conditions (partial pressures of reacting or/and produced gases),
(3) the necessity of precise information on the morphology of the solid, at various stages of the transformation,
(4) the validity of the expression of the rate using equations of the following form:

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

where $A(T, P)$ is not constrained to vary with T according to the Arrhenius law because A does not have the meaning of a rate constant.

Feature (1) implies that the kind of transformation, the initial and the final phases must be known, and eventually the intermediate solid phases must be precisely characterized. This paper concerns only "simple" reactions, i.e. reactions that can be written as $A + \ldots = \nu_B B + \ldots$, where A is a pure solid phase (or possibly belongs to a solid solution, in which case it is the only reacting species of this solution) and B is the only solid phase produced along the entire reaction. These solids are supposed to be roughly stoichiometric. We will see in a further paper the cases of "non-simple" reactions such as competitive and consecutive ones.

Concerning feature (2), it is obvious that the kinetics of chemical transformations of solid compounds may be influenced by temperature (T) and partial pressure of gases (P_i) and that consequently, the rates should be measured in controlled T and P_i conditions. However, it must be acknowledged that the great majority of kinetic analysis relies on experiments done in non-isothermal conditions (in general temperature-programmed heating) and/or under "inert" gaseous atmosphere. The difficulties linked to the kinetic analysis based on mathematical methods applied to the temperature-programmed experiments have already been outlined and discussed in various articles [4–6]. Studies performed with continuous temperature increase have been found to lead to inconsistent data and are thus inadequate to provide information on the mechanism. However some new techniques as temperature-modulated and sample-controlled procedures (CRTA) could prevent from misleading interpretations.

But whatever the experimental procedure could be, it must be emphasized that since the rate very often depends also of the par-

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tial pressures of the gases involved in the reaction balance, the experiments should be done with fixed values of P_i in the gaseous atmosphere. If these conditions are not fulfilled, for example during a dehydration process, the partial pressure in water vapour produced by the solid itself will vary as long as the transformation proceeds, which will in turn affect the measured rate. Moreover, to ensure constant T and P_i (i.e. to assume rapid heat and mass transfer), it appears that the experiments have to be performed with a very small amount of sample (typically less than 10–20 mg). From these considerations, it becomes rather obvious that the best conditions for the measurement of the rate can be achieved in isothermal and isobaric conditions with small amounts of sample.

Feature (3) concerns the characterization of the solid phase which is essential for the assumptions of the kinetic model from which is based the theoretical expression of the rate. For example, the core-shrinking model, assuming that the rate-limiting step of inward growth of the new phase B is located at the A/B interface, leads to different rate equations for spheres, cylinders or plates. More generally, the observation of the morphological changes during reaction is very important since it gives indications on the most suitable kinetic models. Inversely, this makes possible the elimination of some of the rate equations, and gives an idea of the agreement between the hypothetical and real shape of the particles, including the possibility of taking into account a size distribution in the calculation of the rate equation.

Finally, concerning feature (4), it must be recalled that the kinetic rate of a “simple” reaction as previously defined can be expressed by $d\alpha/dt$ (where α is the fractional conversion) provided that the conditions settled during the reaction make it progress within a steady-state. Effectively, if a steady-state is not reached, the concentrations of the intermediate species vary with time and thus it is not possible to define α from any experimental determination of the rate (mass, pressure, etc.). Moreover, the question of the validity of the rate equation in the form of Eq. (1), which is however used by most of the authors in this research domain, has already been discussed in a previous article [7]. An experimental test was proposed which is based on two experiments: in the first one, temperature and partial pressures are maintained constant, whereas in the second one, it is done a jump, or a sudden change, of the temperature, or of the partial pressure of the gases possessing an influence on the kinetic rate. It was clearly shown that in some cases, Eq. (1) was *not valid*, which excludes then the use of all the mathematical methods of kinetic analysis, based on this equation, for the treatment of temperature programmed experiments. Among the reasons that may be involved in the non-validation of Eq. (1), we can find the steady-state assumption, this is why it is important to verify if this assumption can be done. Another reason could be that a rate-limiting step of growth may not exist.

In fact, many investigations were devoted in the past to the determination of the reaction mechanism, often identified to the kinetic model itself due to a particular rate equation (typically R_n, D_n, A_n, etc.) [3]. For decompositions or solid-gas reactions, it is well admitted that two processes are involved in the development of the solid product: nucleation and growth. These processes occur independently one another, since the nucleation involves the surface of the solid, and the growth involves in addition the B phase and the A/B interface between the reactant and the product. Consequently the mechanisms of nucleation and growth are not identical, so that for a given reaction, it will be necessary to access to both mechanisms. As it was postulated for reactions involving a single phase (homogeneous kinetics), the term mechanism must refer to a sequence of elementary steps through which the reactant chemical species are converted in a nucleus of B for the nucleation process, and in chemical species of growing B crystal, for the growth process. The determination of the mechanism of nucleation and growth will be the object of a future article. For the reactions concerned with this paper, the nuclei appear at the surface of the solid phase A and the solid phase has a finite volume, thus all the rate equations based on Avrami’s model assumptions can be excluded (bulk nucleation in an infinite volume).

In Eq. (1), $f(\alpha)$ depends of the shape of the particles (spheres, cylinders or plates). If we except Avrami’s laws, the function $f(\alpha)$ depends of the kind of rate-limiting step of growth (internal interface for R_n laws, diffusion for D_n laws, for example). Then the usual method consists to try all the functions $f(\alpha)$ listed in a table and see what is the best fit with the experimental curves (various mathematical analyses exist based on either isothermal or temperature-programmed experiments). In addition, it is possible to determine the values of the pre-exponential factor and of the apparent activation energy provided that the A term in Eq. (1) follows the Arrhenius law. Some other methods propose to get these values without assuming a particular expression for $f(\alpha)$. In fact, it appears that all these methods are based on the existence of a $f(\alpha)$ function (even when its mathematical form is not made explicit) and thus, on the existence of a rate-limiting step of growth from the beginning to the end of the transformation. However, in order to elucidate with realism the reaction mechanisms, it would be very interesting to verify if the assumption of a rate-limiting step, generally of growth (cf. Section 2) is actually valid.

The aim of the present article is to present experimental tests able to validate both assumptions of steady-state and rate-limiting step of growth. The principle of the tests is first explained, then they are illustrated with several types of “simple” reactions.

2. Principle of the tests

As recalled in Section 1, a “simple” reaction involves two processes, nucleation and growth, both having the same balance equation. Consequently, the kinetic rate, $(d\xi/dt)$, must be the result of both contributions such as

$$\frac{d\xi}{dt} = \left(\frac{d\xi}{dt}\right)_n + \left(\frac{d\xi}{dt}\right)_g \tag{2}$$

where $(d\xi/dt)_n$ and $(d\xi/dt)_g$ are the rates of production of B by nucleation and growth, respectively.

In general, due to the very small size of nuclei, the amount of B produced by nucleation can be neglected besides that due to growth and the measured rate reduces to $(d\xi/dt)_g$:

$$\left(\frac{d\xi}{dt}\right) \approx \left(\frac{d\xi}{dt}\right)_g \tag{3}$$

Let us make a remark with respect to this approximation: when for a powder the nucleation process is a very slow process compared to growth, the measured rate can be given by $(d\xi/dt)_n$ since it can be considered that the particles of A are quasi-instantaneously (totally) transformed in B as soon as a nucleus appears on their surface. The theoretical rate corresponding to this situation can be easily calculated (see Appendix A); in fact we obtain the rate law F1, the so-called “first order” law, for which the word “order” does not possess any “kinetic” meaning. In the following we will refer to reactions corresponding to Eq. (3) (rate-limiting step of growth) although the same methods could be applied to the latter case (rate-limiting step of nucleation).

2.1. Steady-state assumption

In homogeneous kinetics, a steady-state corresponds to a reaction during which the concentrations of the intermediate species are constant; for example, if $[X_i]$ represents the concentration of the ith intermediate, we must have:

$$\frac{d[X_i]}{dt} = 0 \tag{4}$$

Since in solid-state transformations, the intermediate species are created or consumed in interfacial zones (gas/solid or solid/solid interfaces), the amount of X_i, noted n_{X_i}, can be expressed by

$$n_{X_i} = [X_i]e\,s \tag{5}$$

where e and s are the thickness and the area of the corresponding interfacial area. The thickness of the area can be in principle assimilated to one of the dimensions of the crystal cell of the B phase.

Similarly to Bodenstein's approximation on the quasi-steady-states used in homogeneous kinetics, we can define a "pseudo-steady-state" by Eq. (6):

$$\frac{dn_{X_i}}{dt} \approx 0 \quad \text{with} \quad n_{X_i} \approx 0 \tag{6}$$

which gives (using Eq. (5)):

$$s\frac{d[X_i]}{dt} + n_{X_i}\frac{d\,\mathrm{Ln}\,s}{dt} \approx 0 \tag{7}$$

When the reaction proceeds according to a steady-state (Eq. (4)) or a quasi-steady-state ($d[X_i]/dt \approx 0$), Eq. (7) reduces to:

$$n_{X_i}\frac{d\,\mathrm{Ln}\,s}{dt} \approx 0 \tag{8}$$

which will represent the condition for a "pseudo-steady-state" in heterogeneous chemistry, that we use to call "steady-state" in the following. The condition corresponding to Eq. (8) is usually satisfied because the intermediate species (point defects, adsorbed gases, etc.) are most often in small amount and the logarithm of the area of the reaction zones changes less rapidly than the area itself as a function of time.

The principle of the experimental test proposed to validate the steady-state assumption is based on the measurement of the kinetic rate by means of two independent techniques, in general thermogravimetry and calorimetry. It is commonly admitted that the change in mass (Δm) is a measure of the extent of reaction, which gives by derivation versus time the kinetic rate. Moreover the heat flux (dQ/dt) is a direct measure of the kinetic rate. It can be shown that both measurements of the rate are rigorously equivalent if the condition of steady-state is satisfied (see Appendix B). Effectively, since the measurement of the mass change versus time provides us with the kinetic rate of adsorption or/and desorption of one or several gases, it comes obvious that in the case of accumulation of adsorbed species, for example, thermogravimetry will not allow to measure the rate of production in B phase.

Thus the test consists in comparing the kinetic rates measured by thermogravimetry and calorimetry: for steady-state conditions the ratio between them is independent of time, according to Eq. (9):

$$\frac{dQ}{dt} = \frac{\Delta H}{\sum_j M_j \nu_j}\frac{d(\Delta m)}{dt} \tag{9}$$

where ΔH is the enthalpy of reaction, M_j and ν_j, are respectively, the mass and the algebraic stoichiometric number of the gas j involved in the balanced reaction. In addition, due to the scale factor used to superimpose both signals, the test provides us with a measure of the enthalpy of reaction, ΔH. Of course, once the test has been validated, we can define the fractional conversion α, and $(d\alpha/dt) = (1/n_0)(d\xi/dt)_g$ in which n_0 is the initial amount of A.

There exists commercial devices that allow simultaneous thermogravimetry and calorimetry, as for example TG–DSC devices, that can be used in isothermal conditions. Temperature-programmed experiments may also be done in order to know the temperature range over which the steady-state is verified.

2.2. Rate-limiting step of growth assumption

We are interested in the expression of the rate of production of B in the general situation of nucleation and growth in steady-state conditions. If in addition, it is supposed that the growth rate is controlled by an elementary step, then the rate of reaction can be expressed according to the following expression:

$$\frac{d\alpha}{dt} = \phi(T, P_i, \ldots)E(t) \tag{10}$$

where $\phi(T, P_i, \ldots)$ is the areic rate of growth (in mol m^{-2} s^{-1}) which we use to call "areic growth reactivity", and $E(t)$ is in general a function of time (expressed in m^2 mol^{-1}) related to the extent reaction area where the rate-limiting step of growth takes place. If the rate-limiting step is the nth step of a linear mechanism and occurs at an interfacial area, $\phi(T, P_i, \ldots)$ will be expressed by the theoretical expression deduced from the mechanism of growth: $\phi_n(k_n, K_j, P_i, \ldots)$ where k_n and K_j are, respectively, the rate constant of step n (in sense of Arrhenius law) and some equilibrium constants of steps $j \neq n$; $E(t)$ is then the area (per mol) of the corresponding interface. In the case of a rate-limiting step of diffusion between two interfaces, ϕ_n involves D_n, the diffusion coefficient, instead of k_n, and similarly equilibrium constants K_j coming from the concentration of the diffusing species, and $E(t)$ is the product of the area (per mol) of one of the interfaces by a function of the symmetry of the diffusion layer (spherical, cylindrical, or planar).

In Eq. (10), the $E(t)$ function is more general than $f(\alpha)$ in Eq. (1), and similarly, $\phi(T, P_i, \ldots)$ is more general than A in Eq. (1) which is always supposed to follow the Arrhenius law. Eq. (10) holds in all cases provided that a rate-limiting step of growth could be ascertained.

The test that permits to validate the assumption of a rate-limiting step of growth, and consequently the expression of the kinetic rate according to Eq. (10) is called the "ϕE test". It is based on the method of jumps or sudden changes in temperature, or gas partial pressures, as previously explained for the "$f(\alpha)$" test [7]. Here, in a series of experiments conducted up to various values of α_s in same T and P_i conditions, a jump (in temperature or pressure) is done, and the ratios of the kinetic rate after the jump (r_a) to the one before the jump (r_b) are experimentally determined (see Fig. 1). According to Eq. (10), one can see that:

$$\frac{r_a}{r_b} = \frac{\phi(T_a, P_i, \ldots)}{\phi(T_b, P_i, \ldots)} \tag{11}$$

since the terms $E(t)$ are eliminated. Thus the values of the ratios r_a/r_b determined in the various experiments (i.e. for various α_s) must be identical in the range $0 < \alpha_s < 1$. If this is not the case, then there is no possibility to make the assumption of a rate-limiting step for growth, and as a consequence, the use of Eq. (10) and *a fortiori* of Eq. (1) is rigorously forbidden.

Inversely, it may happen that the "ϕE test" would be verified in some special situations as those illustrated in Fig. 2:

- the growth process is kinetically controlled by two elementary steps located in the same reaction zone, for example: molecular adsorption (Fig. 2a) followed by dissociative adsorption (cf. Fig. 2b), adsorption and external interface reaction (cf. Fig. 2c); similarly reactions which occur at external and internal interface with identical dimensions (cf. Fig. 2d);
- all the elementary steps take place in the same reaction zone (same $E(t)$ function); for example if the particles are disinte-

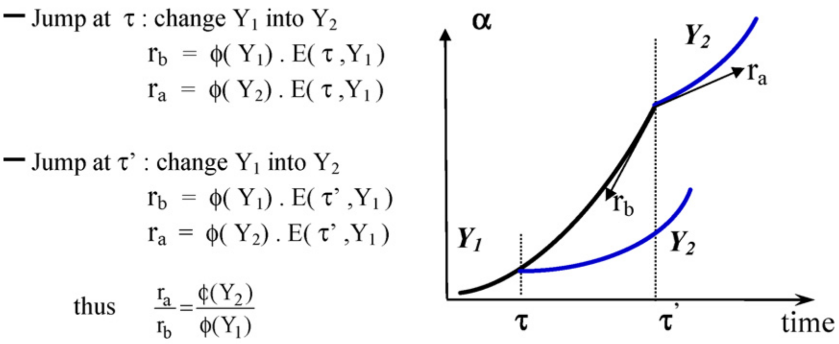


Fig. 1. Jumps done at different values of the fractional conversion (times τ and τ'), and corresponding rates measured after the jump, r_a, and before the jump, r_b.

grated due to cracking after an extensive lattice reorganisation (cf. Fig. 2e), the external and internal interfacial areas involved in the growth process can be practically identical (diffusion is so rapid that it cannot be rate-limiting).

In the next section, we present the results of the "steady-state" and "ϕE" tests for various reactions studied in our laboratory: dehydration of kaolinite, oxidation of magnesium (Mg powder and Mg in solution in liquid AlMg alloy) and of a Zr-based alloy.

3. Application of the steady-state and "ϕE" tests to several solid-state reactions

The steady-state and "ϕE" tests have been applied in our laboratory to various kinds of solid-state reactions among which we have selected a thermal decomposition (Section 3.1), two reactions between gases and solids, either with powder (Section 3.2) or bulk material (Section 3.4), and a reaction between a gas and a liquid (Section 3.3). These examples have been selected for they are representative of different situations with respect to the "steady-state" and "ϕE" tests. It will be shown that even for "simple" reactions, it happened that the "ϕE" test was not validated.

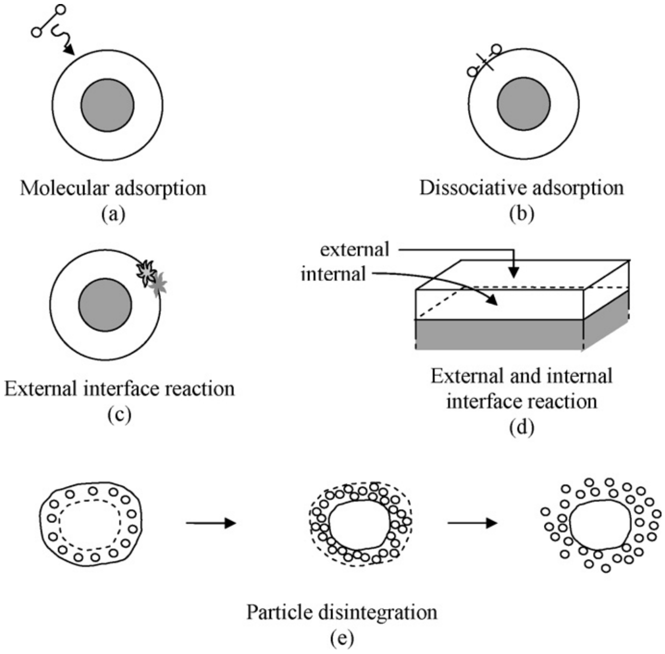


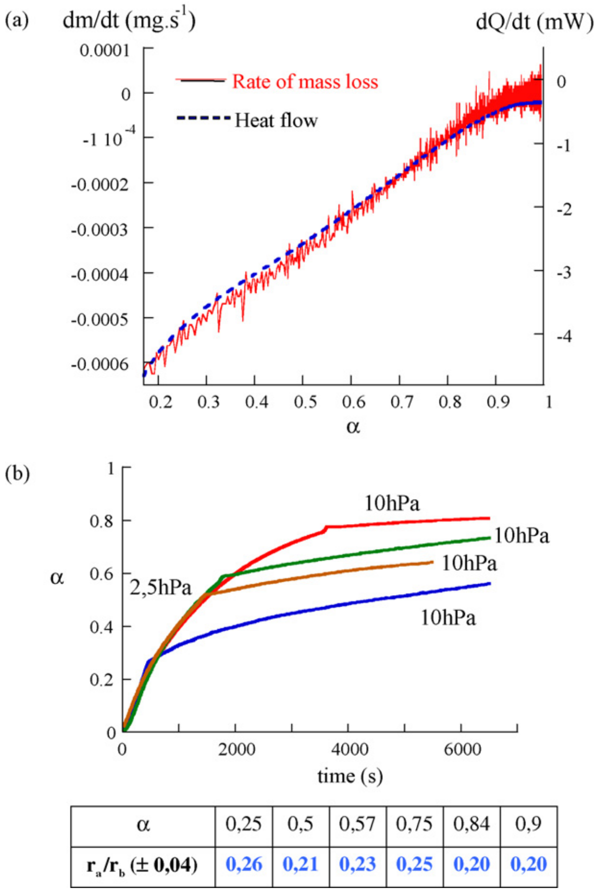
Fig. 2. Scheme illustrating various cases for which the "ϕE" test can be verified.

3.1. Dehydration of kaolinite

The dehydration of kaolinite into metakaolinite corresponds to the following reaction:

$$Al_2Si_2O_5(OH)_4 = Al_2Si_2O_7 + 2H_2O$$

We have studied this reaction at various temperatures and pressures and given a complete description of the kinetics using a model of nucleation and anisotropic growth [8–10]. The experiment for the "steady-state" test has been done using simultaneous calorimetry and thermogravimetry at 973 K and 2.5 hPa in water vapour pressure in helium. The result, shown in Fig. 3a, indicates



α	0,25	0,5	0,57	0,75	0,84	0,9
r_a/r_b (± 0,04)	0,26	0,21	0,23	0,25	0,20	0,20

Fig. 3. Thermal dehydration of kaolinite at 973 K: (a) steady-state test (2.5 hPa in H_2O) and (b) kinetic curves $\alpha(t)$ with pressure jumps from 2.5 to 10 hPa and values of the rate ratios.

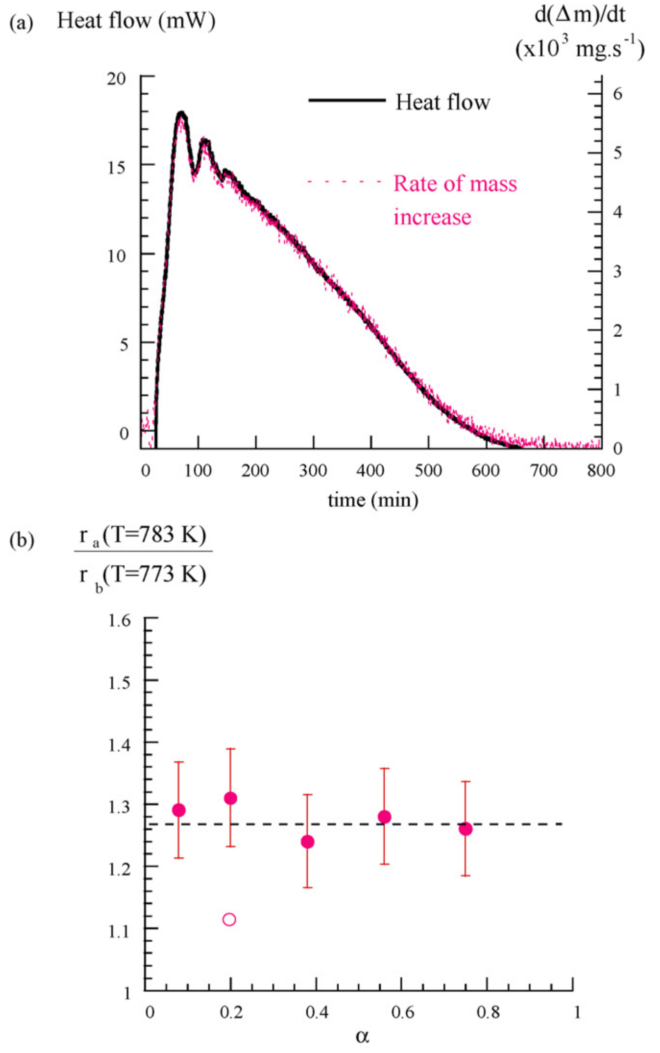


Fig. 4. Oxidation of Mg into MgO by oxygen at 783 K: (a) steady-state test (0.2 kPa in O_2) and (b) "ϕE" test with temperature jumps from 773 to 783 K.

that the test is validated since the curves of heat flow and mass loss rate can be rather well superimposed in the range of α between 0 and 1.

Moreover, it can be seen in Fig. 3b that the values of the ratios of the rates at various values of α are approximately equal, which means that the "ϕE test" is also validated. The kinetic curves observed in Fig. 3b well illustrate the effect of the jumps (here the water vapour pressure was suddenly changed from 2.5 to 10 hPa) on the kinetics.

3.2. *Oxidation of a magnesium powder*

An other interesting example is that of the oxidation of Mg into MgO by oxygen for which the initial large particles (~400–500 μm) were disintegrated since after reaction a fine powder was obtained with a specific surface area equal to 50 $m^2 g^{-1}$ (particle diameter ~50 nm) [11,12]. This is a common phenomenon which happens when it exists some difference between the molar volumes of the solid reactant and product (the oxide/metal ratio is equal to 0.81 in the present case). Fig. 4a and b show the result of the steady-state and "ϕE" tests, respectively. Both are clearly validated, which seems surprising if one considers the important morphological changes during the reaction. In fact, we could explain this behaviour by means of a kinetic model (R3 law type adapted to a cylindro-spherical geometry) with a rate-limiting step of growth located at the external interface (i.e. the surface of the contracting Mg particles since the MgO particles are continuously ejected, as shown in Fig. 2e). In fact, the function $E(t)$ takes the same expression than if the oxide formed a dense layer around the metal core. Hence, in this case, important changes in the morphology of the solid particles do not have any consequence on the rate-limiting step of growth.

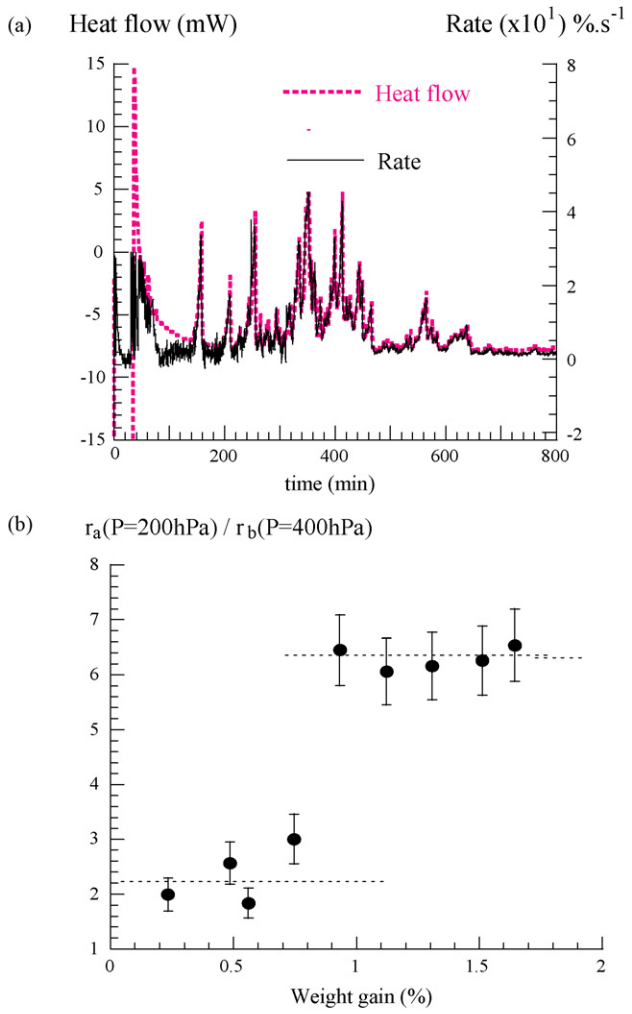


Fig. 5. Oxidation of Mg in Al–Mg 5% in the liquid state into MgO by oxygen at 973 K: (a) steady-state test (0.2 kPa in oxygen) and (b) "ϕE" test with oxygen pressure jumps from 4.0 to 2.0 kPa (circles) and from 2.0 to 4.0 kPa (squares).

3.3. *Oxidation of a liquid Al–Mg alloy*

This case consists of a very unusual situation in the domain of oxidation of alloys since gaseous oxygen reacts with AlMg in the liquid state. The selective oxidation of Mg into MgO, from a liquid Al–Mg 5% alloy has been studied at 973 K under controlled oxygen partial pressure [12]. The results of the steady-state and "ϕE" tests are reported in Fig. 5a and b. It can be seen that the curves are very irregular, which was attributed to rapid and important morphological changes during the reaction. As these changes differed from an experiment to another, the kinetic curves were not reproducible. However the result of the steady-state test for the oxidation of Mg (in solution into liquid alloy) into MgO shows that the steady-state approximation seems to be valid (cf. Fig. 5a).

Considering the "ϕE" test illustrated by Fig. 5b, it was surprising to find two distinct domains of fractional conversion in which the test was verified. The rates ratio was approximatively constant for $0 < \alpha < 0.2$ and then for $0.3 < \alpha < 0.52$, but the ratio value changed from about 2 to 6.5 from the first domain to the second one. It is interesting to notice that, even if the kinetic curves were not reproducible, the ratios of the rates measured from the pressure jumps were well reproducible (cf. Fig. 5b). Moreover, similar values were obtained whatever could be the sense of the oxygen pressure jumps, from 2.0 to 4.0 kPa or from 4.0 to 2.0 kPa (squares and circles of Fig. 5b).

An other interesting feature of this reaction is that the activity in Mg in the liquid alloy, a_{Mg}, varies as α increases, so the constancy of the ratios r_a/r_b indicates that either ϕ is independent of a_{Mg}, or ϕ can be written as

$$\phi(T, P_{O_2}, a_{\mathrm{Mg}}) = f(a_{\mathrm{Mg}})g(P, T) \qquad (12)$$

i.e. a_{Mg} is a separate variable of the growth rate. Thus, the method may lead also to interesting results concerning the form of the expression of the reactivity of growth.

More details can be found in Refs. [12,13] concerning the origin of the two domains of validation of the "ϕE" test. To summarize, these have been attributed to two kinds of adsorbed oxygen, probably due to differences in morphology of MgO particles from the first domain to the second one. This result points out the interest of validating the "ϕE" test before searching for a theoretical expression of the kinetic rate when one wants to fit the kinetic data.

3.4. Oxidation of a Zr-based alloy by oxygen or water vapour

Because of their use in PWR nuclear reactors, the resistance towards oxidation of Zr based alloys has been extensively studied. When oxidized by oxygen or water vapour, the kinetic curves exhibit a break-away attributed to morphological changes in the oxide scale (pores, cracks) and called the "kinetic transition". We have studied these reactions with the objective of detect any change in the mechanism of ZrO_2 growth before and after the kinetic transition.

The most interesting results were those of the "ϕE" test which indicated in the pre-transition stage the existence of a rate-limiting step before the kinetic transition, and a change in the mechanism after the kinetic transition [14,15]. Fig. 6a and b reports the results obtained with Zircaloy-4 in the case of the oxidation at 823 K by water vapour at 13 hPa. Fig. 6a clearly shows that a steady-state is established during the pre-transition stage since both curves of heat flow and rate of mass increase are very well superimposed. After the kinetic transition, the signals are not so well superimposed, however with a slight change in the scale factor, it is possible to have a reasonably good agreement. Fig. 6b presents the results of two kinds of jumps done for the "ϕE" test, temperature and pressure jumps. It appears that before the kinetic transition, the ratio of the rates obtained with the temperature jumps is practically constant with a mean value of 2.32; then at the kinetic transition, this ratio decreases and it does not take a constant value during all the post-transition stage. It means that the assumption of a rate-limiting step of growth of the oxide scale can be done only before the kinetic transition. Moreover, in the pre-transition stage, the water vapour pressure has no effect on the kinetic rate, whereas the ratios obtained from the jumps in water vapour pressure are not constant (cf. Fig. 6b: pressure jumps), which confirms that in the post-transition stage, the mechanism is different. So the morphological changes in the oxide scale not only induce a change in the kinetic rate, but also modify the mechanism of reaction (after the kinetic transition, the expression of the rate is not of the form ϕE).

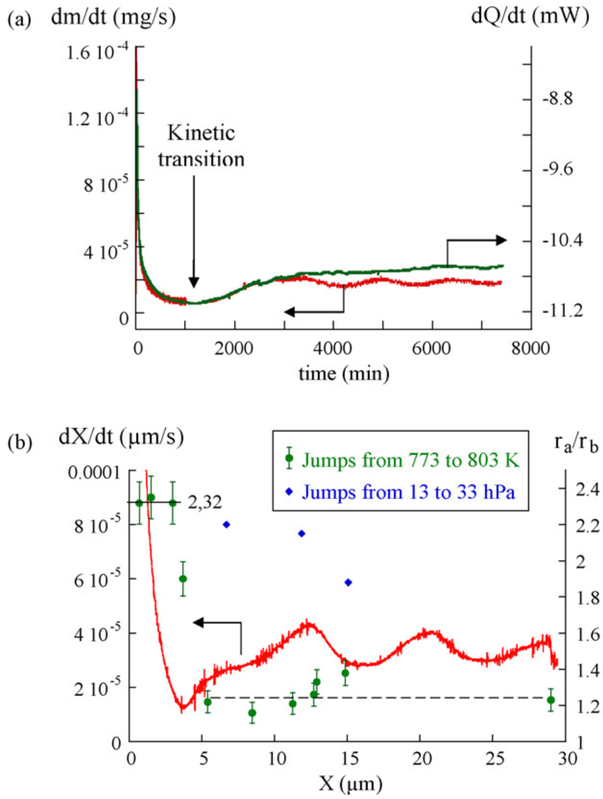


Fig. 6. Oxidation of Zircaloy-4 at 823 K by water vapour (water vapour pressure: 13 hPa; hydrogen pressure: 10 hPa): "ϕE" test with temperature jumps from 773 to 803 K and pressure jumps from 13 to 33 hPa.

More details on the elementary steps of the oxide growth mechanism can be found in Refs. [14,15].

4. Conclusions

It has been shown that simple experiments allow to validate important assumptions for the kinetic analysis of solid-state reactions. Several examples of reactions have been presented illustrating the interest of the "steady-state" and the "ϕE" tests. These tests may be very useful before any attempt of kinetic modelling. In particular, they can be used to identify the range of α in which it will be possible to find a kinetic model based on the assumption of a rate-limiting step. Moreover it indicates if the rate equation can be expressed by the product of two functions $\phi(T, P_i, a_i, \ldots)$ and $E(t)$, and may give interesting information on the ϕ function. In case of important modifications of the morphological properties of the solid during the transformation, it will also be possible with the ϕE test to know if these changes have an effect or not on the kinetic rate. Finally these tests may allow to settle the basis of a kinetic modelling even in the case of non-reproducible experiments, due to the method of jumps.

Then, as recalled in Section 1 and previously published, it is also possible to use the "$f(\alpha)$" test [7] to discriminate between kinetic models those for which the $E(t)$ function may be formulated as a $f(\alpha)$ function.

Using the "$f(\alpha)$" test, the "steady-state" test and the "ϕE" test, which represents a relatively low number of experiments (about 10 more or less), one is able to get a verification of the basic assumptions on which most of the kinetic analyses are based; in our opinion, this appears to be necessary before searching an appropriate rate equation for the kinetic modelling.

Appendix A. Calculation of the rate of reaction which transforms a powder A into B with slow nucleation and instantaneous growth (F1 law)

A.1. Assumptions

- as soon as a nucleus appears on the surface of a grain, its transformation is complete and instantaneous,
- the nucleation process is characterized by the areic nucleation frequency γ (i.e. the number of nuclei per unit of surface), which is supposed to be constant for isothermal and isobaric conditions,
- the rate-limiting step of nucleation is supposed to be located at the surface of the grains.

Notations:

γ	the areic nucleation frequency ($\mathrm{m^{-2}\,s^{-1}}$)
v_{0_A}	the initial volume of a grain of phase A ($\mathrm{m^3}$)
s_0	the initial surface of a grain of phase A ($\mathrm{m^2}$)
S_0	the total initial surface of phase A ($\mathrm{m^2}$)
$S_L(t)$	the total surface of phase A at time t ("free surface" for nucleation, $\mathrm{m^2}$)
N_0:	the initial number of grains of phase A
n_0:	the initial amount of phase A (moles)

During the time dt, the number of grains of phase A that are totally transformed is equal to the number of nuclei appeared in the powder, i.e. $\gamma S_L(t)\,\mathrm{d}t$. Thus the amount d$\xi$ of A having reacted during dt is proportional to dt according to Eq. (A.1.1):

$$\mathrm{d}\xi = \gamma S_L(t)\frac{v_{0_A}}{V_{m_A}}\mathrm{d}t \tag{A.1.1}$$

A.2. Calculation of $S_L(t)$:

The decrease in the free surface for nucleation during dt is equal to the product of the number of grains having reacted ($\gamma S_L\,\mathrm{d}t$) by the surface of a grain s_0:

$$\mathrm{d}S_L = -\gamma S_L s_0\,\mathrm{d}t \tag{A.1.2}$$

which leads by integration to

$$S_L(t) = S_0 \exp(-\gamma s_0 t) \tag{A.1.3}$$

A.3. Calculation of the rate

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{1}{n_0}\frac{\mathrm{d}\xi}{\mathrm{d}t} = \frac{\gamma v_{0_A} S_0}{n_0 V_{m_A}}\exp(-\gamma s_0 t) \tag{A.1.4}$$

Since $(n_0 V_{m_A}/v_{0_A}) = N_0$ and $S_0 = s_0 N_0$:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \gamma s_0 \exp(-\gamma s_0 t) \tag{A.1.5}$$

From Eq. (A.1.5) we obtain:

$$\alpha = 1 - \exp(-\gamma s_0 t) \tag{A.1.6}$$

and

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \gamma s_0 (1-\alpha) \tag{A.1.7}$$

Eq. (A.1.7) corresponds to the law F1 mentioned in the literature, usually called the first-order law. Here it can be seen that the kinetic constant γs_0 takes a physical meaning.

Appendix B. The proportionality between the rates determined from the mass variation and from the heat flow

Notations

n_0	initial amount of the initial phase A
Δm	mass variation
ν_G	algebraic stoichiometric number of gas G involved into the reaction balance
M_G	molar mass of gas G
H	enthalpy of reaction

B.1. Expression of the rates in steady-state conditions

The rate of mass variation in steady-state conditions can be expressed by Eq. (A.2.1):

$$\frac{\mathrm{d}(\Delta m)}{\mathrm{d}t} = -n_0\frac{\mathrm{d}\alpha}{\mathrm{d}t}\sum_G \nu_G M_G \tag{A.2.1}$$

The heat flux produced or consumed in steady-state conditions can be expressed by Eq. (A.2.2):

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = n_0\frac{\mathrm{d}\alpha}{\mathrm{d}t}H \tag{A.2.2}$$

It is very easy to see that at any time of reaction, the ratio of the rates takes a constant value:

$$\frac{(\mathrm{d}(\Delta m)/\mathrm{d}t)}{(\mathrm{d}Q/\mathrm{d}t)} = \frac{\sum_G \nu_G M_G}{H} \tag{A.2.3}$$

From this constant of proportionality, one may find the value of the enthalpy of reaction H.

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