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# PHENOMENOLOGICAL KINETICS
## An alternative approach

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## Abstract

Traditional phenomenological kinetics describes the process rate in terms of the progress degree (mass fraction which has already undergone the change), $\alpha$, and with a monomial function (or combination of monomial functions for multistep processes) of $(1-\alpha)$, without any connection to the underlying mechanism at the molecular level.

The approach proposed in the present work aims at the direct treatment of the experimental data, like DSC records, without suggesting any specific reaction mechanism and excluding any Arrhenius like behaviour. Formal expressions are proposed that include the thermodynamic constraints for any spontaneous process, viz. a negative drop of the Gibbs function throughout the process, and describe the process rate as the result of the effects of a thermodynamic driving force, identified with the drop of the Gibbs function, and of the medium hindrance.

**Keywords:** general expressions, phenomenological kinetics, physical meaning

## Introduction

Phenomenological kinetics describes the overall progress of a transformation with simple linear differential equations, where the process rate is expressed in terms of the progress degree (mass fraction which has already undergone the change), $\alpha$, and is a monomial function (or combination of monomial functions) of $(1-\alpha)$, without any connection to the underlying mechanism at the molecular level. The usual expressions look like:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=\dot{\alpha}=k_{\mathrm{n}}(1-\alpha)^{\mathrm{n}} \qquad (1)$$

Equation (1) holds for constant-temperature conditions. Every effect of temperature concerns the kinetic constant, $k_{\mathrm{n}}$, while the kinetic order, $n$, is supposed to remain unaltered. Equations of this kind are normally used for chemical reactions, but also apply to a number of transformations that do not involve any chemical change and can be simply referred to as processes from the state **A** toward the state **B**.

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In the case of simple reactions in the gaseous state Eq. (1) corresponds to a well defined reaction mechanism, namely, binary collisions which are described with the Maxwell–Boltzmann statistical mechanics. When so, one can easily find that:

$$n=2$$

and

$$k_n=k_2\approx k_0\exp(-\Delta E^*/RT) \tag{2}$$

where the term $k_0$ conceals a number of parameters, like size of the reacting molecules, average number of binary collisions per unit time and unit volume, orientation of the impact trajectories, etc., and $\Delta E^*$, called 'activation energy', is the energy threshold that allows the potentially reacting molecules to be 'singled out' from the whole population of the reagent species. The overall description of a simple reaction in the gas state is well known as 'theory of the absolute velocity of reaction' by Eyring [1]. Cases where $n\neq 2$ deserve special mechanisms [2] since the simple 'activated' collision can no longer account for the experimental evidence: combinations of bimolecular steps (these too in the gas state) allow a reasonable description of the actual reaction path.

In spite of such very restricted range of applicability, Eqs (1) and (2) have been successfully used to describe practically every time-dependent process, including those in solid and liquid viscous media, since the corresponding fits of $\alpha$ *vs.* $t$ (where $t$ stands for time) and $\log(k_n)$ *vs.* $1/T$ (in the so called Arrhenius plot) trends appear satisfactory. The $n$ and $\Delta E^*$ values drawn from such fits are however devoid of any physical meaning and should therefore be used with some caution when data from different authors (or experimental runs) are to be compared to one another.[**]

The serious mismatch between the poor physical reliability of the simplistic Eqs (1) and (2) and their overspread use and success remains to be explained on the basis of well established physical principles. It is a matter of fact that the kinetics of a given process within a complex system, i.e., in the presence of many compounds, many phases, that imply inter-compound and/or inter-phase interactions, may be affected by transformations which depend on the progress of the process, but do not directly contribute to the specific experimental evidence recorded to evaluate the process rate, namely, concentration values, intensity of some spectrum bands, areas beneath a calorimetric (either IC or DSC) signals, which are strictly related to some specific compound that is undergoing the change. In a phenomenological approach these side changes may be viewed as 'perturbations' which can substantially affect the rate of the process studied. For this reason, the fit of the experimental data with expressions like Eq. (1), although satisfactory according to the regression analysis, may be misleading since any change that does not directly concern the experimental evidence is concealed within a 'kinetic constant', $k_n$, that is assumed not to depend on the progress degree, $\alpha$.

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[**] A worth mentioning, subtle and not always recognized source of mistake concerns the Arrhenius fits: the values of $k_0$ and $\Delta E^*$ are auto-correlated, namely, different ($k_0$, $\Delta E^*$) couples can be drawn for similar data sets. The larger the $\Delta E^*$ value, the larger the corresponding $k_0$.

The necessity of predicting or interpreting the kinetics of processes that take place in batch or continuous reactors has been faced by assuming some reaction mechanism [3] which may include non-chemical steps, like diffusion of reactants and products, or by developing mathematical functions [4] which can represent the experimental data. Splitting the mechanism of the process in many elementary steps (which are treated with the traditional approach) implies the involvement of intermediate compounds (or states) which should be, at least qualitatively, verified through chemical and/or physical analyses of the system: sometimes this is not possible and other 'tricks', mainly based on mass and/or charge balances, have to be introduced [4]. The eventual result of these approaches is therefore a shift of the attention toward the implementation of mathematical methods to solve systems of differential equations. It can be therefore concluded that these approaches are of technological interest as far as they provide some rationale for the management of plants, but do not contribute to improve the basic understanding of chemical kinetics, since they overcome the intrinsic difficulties of interpretation. For example, these models assume that the molecularity of a reaction, i.e., the number of molecules involved in each single 'elementary' reaction step, has to correspond to the relevant kinetic order. This assumption can be accepted for bimolecular reactions in the gaseous phase, since it is the simplest way to describe binary collisions, but is rather untenable for transformations within condensed media. Further 'elementary' steps included in the model can eventually lead to an apparent overall kinetic order that has nothing to do with the collision of two molecules, e.g., $n \neq 2$ or $n$=non-integer number, but $n$ still remains an intrinsic character of the reaction mechanism, without any reference to the possible effects related to the changes of the surrounding medium.

At the other extreme are found attempts to simulate the actual reaction mechanism by MD computations [5]. These are very interesting, but still limited to micro-systems and of little help for quantitative descriptions of real processes.

Some alternative approaches have been recently proposed. The one by Sempere, Nomen and Serra [6] aims at directly using experimental data, viz., $\alpha(t)$ at various $T$, arranged in matrix arrays that can be algebraically manipulated to single out orthonormal vectors separately accounting for the $\alpha$ progress and the effect of temperature changes. This approach therefore assumes a thorough independence between the main variables, viz., $\alpha$ and $T$, which is already implicit in the traditional kinetic expressions like Eq. (1). The great advantage of this approach is that it does not assume any specific mechanism (which therefore makes the formal expressions suitable to a wide range of cases) and allows for temperature effects that may be formally different from the traditional Arrhenius expression.

More theoretical and general is the aim of Šesták's approach [7] which suggests a description of the reaction dynamics in solid phases in terms of generalized forces and fluxes, but cannot offer ready-to-use ways to overcome the tremendous mathematical difficulties.

The approach proposed in the present work occupies an intermediate position between those mentioned above [6, 7] in as much as it aims at keeping the simplicity of the traditional expressions, which are however given an unambiguous meaning and a rationale for their correct use. It allows a direct treatment of the experimental data without suggesting any specific reaction mechanism and excluding any Arrhenius like behavior. It includes the thermodynamic constraints for any spontaneous process, viz. a negative drop of the Gibbs function throughout the process, and is based on the assumption that the process rate may referred to as the result of the effects of a thermodynamic driving force, identified with the residual drop of the Gibbs function, and of the medium hindrance which can change in the course of the process.

## Isothermal kinetics

One can easily recognize that neither Eqs (1) nor (2) is related to the thermodynamic necessary condition for the progress of a given transformation within a statistically macroscopic system, namely, a negative drop of the corresponding Gibbs function, $\Delta_r G \leq 0$, which has to be met throughout the process.

The value of the function $G$ of the reacting system depends on temperature, $T$, pressure, $p$, and system composition: for the present purposes, composition can be replaced with the mass fraction that has already undergone the process A→B, namely the progress degree, $\alpha$.

When $dT=0$ and $dp=0$, $G$ is a function of $\alpha$, which is in turn a function of the time, $t$,

$$G[\alpha(t)]=(1-\alpha)G(\text{A})+\alpha G(\text{B})+\Delta G_{\text{mix}} \tag{3}$$

where $\Delta G_{\text{mix}}$ is the $G$ change that accounts for the mixing of reagents and products.

This term may however be neglected being much smaller than the other two. For $t=0$, $G=G(\text{A})=G(\alpha=0)$, while for $t=\infty$, $G=G(\text{B})=G(\alpha=1)$. The reaction $G$ drop is:

$$\Delta_r G[\alpha(t)]=G(\text{B})-G[\alpha(t)]=[G(\text{B})-G(\text{A})](1-\alpha)=(1-\alpha)\Delta_r G_0 \leq 0 \tag{4}$$

where $\Delta_r G_0=[G(\text{B})-G(\text{A})]$.

For a phenomenological description of the process one can assimilate the process rate ($d\alpha/dt$) to a generalized flux sustained by a generalized driving force (terms drawn from the Thermodynamics of Irreversible Processes [8,9]) with the assumption of a linear behavior. The driving force that sustains the reaction progress is $-\Delta_r G[\alpha(t)]$. When $\Delta_r G[\alpha(t)]$ vanishes, a further reaction progress becomes impossible (Fig. 1).

One therefore can state that:

$$\dot{\alpha}=\{-\Delta_r G[\alpha(t)]\}\{k[\alpha(t)]\}=-k[\alpha(t)]\Delta_r G_0(1-\alpha) \tag{5}$$

It is easy to recognize that $k[\alpha(t)]$ has dimensions of [energy$^{-1}$ mol time$^{-1}$] and therefore those of $(1/k[\alpha(t)])$ are [viscosity/density], viz., [cinematic viscosity]; $(1/k[\alpha(t)])$ can be then referred to as the hindrance (and its reverse, $k[\alpha(t)]$, to as the compliance) of the medium with respect to the progress of the transformation. The assumption of a medium compliance that can depend on $\alpha(t)$ meets the sake of generality, accounting also for cases where the medium compliance does not change with $\alpha$.

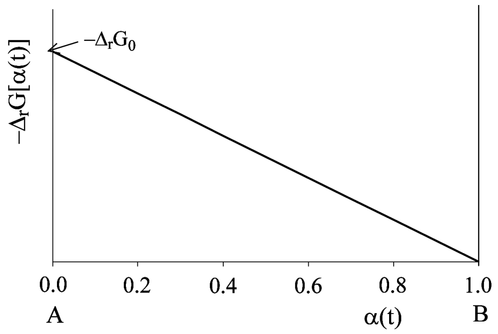

**Fig. 1** Driving force of the reaction throughout the range of the progress degree

Equation (5) is still completely phenomenological, but has the advantage of including the thermodynamic constraints directly into the expression for the process rate.

One can now reproduce the same relationships drawn for reactions in the gaseous state suggesting naïve expressions for $k[\alpha(t)]$, such as,

$$k[\alpha(t)]=k_n[1-\alpha(t)]^{(n-1)} \tag{6}$$

where $n\geq 0$ could be given also non integer values. Accordingly, when the 'experimental' kinetic order is $n=0$, $n=1$ and $n=2$, the corresponding medium compliance and process rate are those reported in Table 1.

**Table 1** Simple expressions for the medium compliance and process rate that meet experimental integer values of the apparent kinetic order

| Medium compliance | Process rate | Apparent kinetic order |
|---|---|---|
| $k[\alpha(t)]=k_0/(1-\alpha)$ | $(d\alpha/dt)=-(k_0\Delta_r G_0)$ | $n=0$ |
| $k[\alpha(t)]=k_1$ | $(d\alpha/dt)=-(k_1\Delta_r G_0)(1-\alpha)$ | $n=1$ |
| $k[\alpha(t)]=k_2(1-\alpha)$ | $(d\alpha/dt)=-(k_2\Delta_r G_0)(1-\alpha)^2$ | $n=2$ |

These expressions are formally equivalent to Eq. (1), but imply an apparent kinetic order related with both driving force and medium compliance. In other words, the kinetic order is not an intrinsic property of the process considered, since it can change when the medium is changed. This way of describing the process rate can be of help when viscous and heterogeneous media are considered, or for processes, like phase transitions, depletion of solutes, microbial growth, etc., that do not directly deal with chemical transformations. In these cases, however, one can be obliged to assume more complex expressions for $k[\alpha(t)]$, such as, for instance, polynomial functions,

$$k[\alpha(t)]=\sum_{n\geq 0} k_n[1-\alpha]^{(n-1)} \tag{7}$$

and for the process rate,

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right) = -\Delta_{\mathrm{r}} G_0 (1-\alpha) \sum_{\mathrm{n}\geq 0} k_{\mathrm{n}} (1-\alpha)^{(\mathrm{n}-1)} \tag{8}$$

The simple case where the sum in Eq. (8) can be truncated at the second term describes a situation where the ‘experimental’ kinetic order changes from 0 to 1 and again to 0 in the course of the process (Fig. 2 where $K_{\mathrm{obs}}$ is the apparent kinetic constant observed in a given $\alpha$ range).

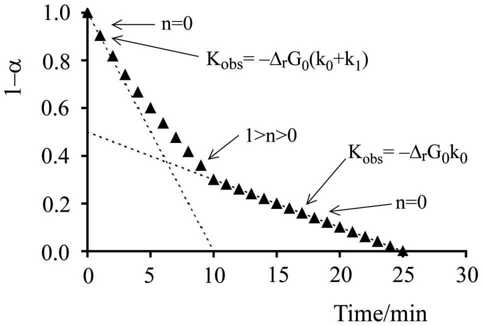

**Fig. 2** A hypothetical case where the apparent kinetic order, *n*, depends on $\alpha$

Changes of the ‘experimental’ kinetic order along the course of a transformation can be found in every field of applied chemistry and are interpreted as the phenomenological result of an underlying complex mechanism that implies several intermediate steps between the initial and final state of the system. It must be noticed that these steps mostly deal with assumed events at the molecular level, whereas the experimental findings often concern the macroscopic or mesoscopic scale. Once again such interpretations may be likely for processes in the gaseous state or in diluted solutions, but seem rather unreliable in many other conditions, where changes of the medium physical properties can be of paramount importance. For example, the number of accessible active sites of heterogenous catalysts can change in the course of the reaction being occupied by product molecules; many processes dealing with nanotechnologies are governed by the dispersion of the reaction medium, which can be dramatically affected by the progress of the reaction itself. In these cases, at the price of a poorer information about the real history experienced by the system, the phenomenological approach has to be preferred, provided that it can include the concurrent changes of the medium, as implicitely stated by Eq. (5).

More in general, Eq. (5) suggests that $k[\alpha(t)]$ can be empirically approached as

$$k[\alpha(t)] = \frac{1}{\Delta_{\mathrm{r}} G_0} \frac{\mathrm{d}\ln F(t)}{\mathrm{d}t} \tag{9}$$

where $\mathrm{F}(t)$ is any suitable fitting expression for the $(1-\alpha)$ *vs.* $t$ experimental trend and $\Delta_{\mathrm{r}}G_0$ is calculated from literature values of $G(\mathrm{A})$ and $G(\mathrm{B})$.

The reader can easily find many case studies in his/her own field where Eq. (9) can be directly applied. Being involved since many years in the applications of calorimetry and thermal analysis in food science, it is easier for me to provide an example from my own experience, namely, the 'gelatinization' of starch in excess water. This process is indeed very complex as far as it involves a number of events which can be roughly summarized as follows: starch granules are swollen by the diffusing water, amylopectin crystal arrays loose their ordered allignment, an interpenetrated mixed amylose/amylopectin gel is formed, where amylose undergoes a fast but rather incomplete crystallization. When studied by means of isothermal calorimetry, starch gelatinization produce a signal like that reported in Fig. 3 (data from [11]).

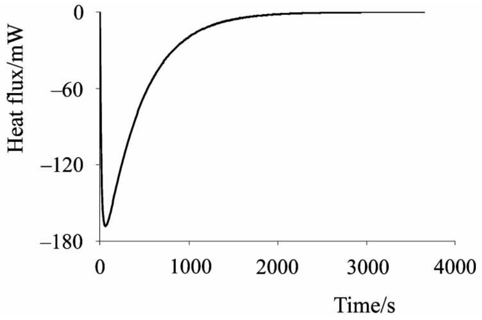

**Fig. 3** Gelatinization of starch. Isothermal calorimetry record obtained at 95°C with a Setaram C80 calorimeter operating with a two-chamber cell: the record starts when the hot water is poured from the upper chamber into the lower one containing few dry rice kernels [11]

When the record is scaled [10, 12] by a damping factor, exp(–τ/*t*), to account for the time constant, τ, of the calorimeter, the resulting profile, d*Q*/d*t*, corresponds to the product $[\Delta_r H(\mathrm{d}\alpha/\mathrm{d}t)]$, where $\Delta_r H$ is the overall enthalpy of the process that is given by the total area underlying the signal. Straightforward routines give the (dα/d*t*) *vs.* (1–α) and the (1–α) *vs. t* trends (Fig. 4). In this case $\Delta_r G_0$ concerns two different physical states of rice kernels (namely, before and after starch gelatinization), where also other concurrent processes, like protein denaturation and water displacements, take place which involve poorly detectable calorimetric effects but none the less produce dramatic changes of the texture of the product and therefore are expected to affect the progress of starch gelatinization.

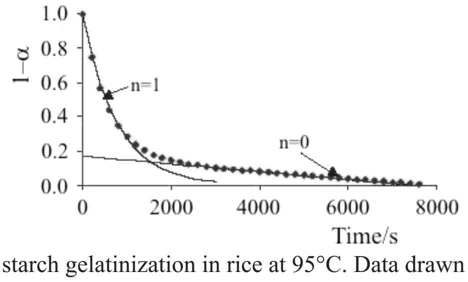

**Fig. 4** Progress of starch gelatinization in rice at 95°C. Data drawn from the record reported in Fig. 3. The use of classical kinetic equations shows a change of the apparent kinetic order in the course of the process

The best fit of these data with standard kinetic expressions can be obtained attributing a first and zero order trend to the early and the end phase of the process, respectively. A more reliable output is instead produced by applying Eq. (9) which indeed shows that the whole process takes place in a medium the compliance of which changes with α (Fig. 5). Although $\Delta_r G_0$ cannot be evaluated, it must be referred to as a constant quantity in the isothermal conditions considered; the declining trend of $k[\alpha(t)]\times\Delta_r G_0$ reported in Fig. 5b therefore concerns only the $k[\alpha(t)]$ term and indicates that starch gelatinization takes place within a medium the compliance of which changes in the course of the process.

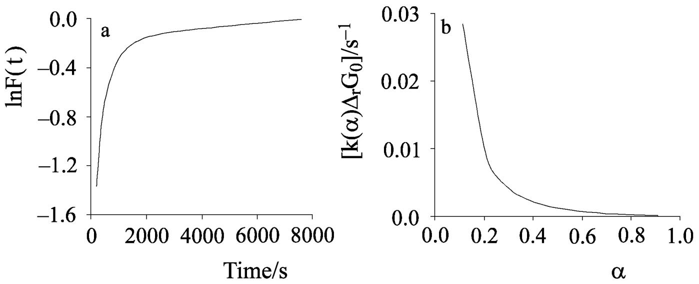

**Fig. 5** Treatment of the above data according to Eq. (9). a – trend of ln*F*(*t*), i.e. ln(1–α), *vs*. time, b – trend of the same function *vs*. α

The analysis of the isothermal trend of $\dot{\alpha}=\dot{\alpha}(\alpha)$ reveals that such a function is usually decreasing at any temperature, save for the cases with an apparent $n=0$. The derivative of $\dot{\alpha}$ with respect to α (Eq. (5)) is:

$$\begin{aligned}\frac{\mathrm{d}\dot{\alpha}}{\mathrm{d}\alpha}&=\Delta_r G_0 k_n(\alpha)-\Delta_r G_0(1-\alpha)\frac{\mathrm{d}k_n(\alpha)}{\mathrm{d}\alpha}=\\&=\Delta_r G_0\left[k_n(\alpha)-(1-\alpha)\frac{\mathrm{d}k_n(\alpha)}{\mathrm{d}\alpha}\right]=\\&=\Delta_r G_0\sum_{n\geq 0}nk_n(1-\alpha)^{(n-1)}\leq 0\end{aligned}\tag{10}$$

where, for the sake of generality, Eq. (7) has been assumed and account has been taken for the $\Delta_r G_0<0$ condition. Thence in any case $(\mathrm{d}\dot{\alpha}/\mathrm{d}\alpha)\leq 0$ has to be found.

Many processes of practical interest, like consecutive and enzymatic reactions, imply some intermediate step between starting and ending state. These cases can be formally described through the same approach presented above by replacing the progress degree of each step with some mass fractions (Appendix).

## Effects of temperature changes

The idea underlying the above description of isothermal processes directly implies that the effect of temperature changes on the process rate cannot have the simple form of the Arrhenius equation. Equation (5) indeed contains the term $\Delta_r G_0$ whose temperature derivative is $-\Delta_r S_0$ and therefore has to be represented as:

$$\Delta_r G_0(T) = \Delta_r G_0(T_0) - (T - T_0)\Delta_r S_0(T_0) - \int_{T_0}^{T} \mathrm{d}T \int_{\theta=T_0}^{\theta} \Delta_r C_p(\theta) \frac{\mathrm{d}\vartheta}{\theta} \qquad (11)$$

where $\Delta_r C_p = [C_p(\mathrm{B}) - C_p(\mathrm{A})]$, is the relevant difference of the heat capacities.

A main point to be raised is that any increase of $T$ cannot be instantaneous and would therefore produce some uprising of $\alpha$, since $\alpha = \alpha[T(t)]$.

Once achieved the above integration, the driving force, $\Delta_r G_0(T)\{1 - \alpha[T(t)]\}$, can be evaluated from the experimental $\alpha[T(t)]$ trend determined with DSC investigations (or any other suitable technique), namely sweeping the area beneath the DSC signal. A suitable expression for $k\{\alpha[T(t)]\}$ can be finally obtained dividing the profile of the DSC signal by the driving force.

The kinetic interpretation of DSC traces deserve some qualitative considerations that are related to the state $\alpha=0$, namely the 'initial' rate of the process; any else 'iso – $\alpha$' condition along the reaction coordinate (namely when $\alpha>0$) would indeed be arbitrary and/or of ambiguous physical meaning. When $\alpha=0$, Eq. (5) becomes

$$\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha=0} = \dot{\alpha}_0 = -k_0 \Delta_r G_0 \qquad (12)$$

with $k_0 = \sum_{n\geq 0} k_n$, (with reference to Eq. (7)), which allows a direct evaluation of $k_0$ once the initial rate and $\Delta_r G_0$ are known. By deriving one obtains:

$$\left(\frac{\mathrm{d}\dot{\alpha}_0}{\mathrm{d}T}\right) = k_0 \Delta_r S_0 - \Delta_r G_0 \frac{\mathrm{d}k_0}{\mathrm{d}T} \qquad (13)$$

and can envisage two main situations for the $|\Delta_r G_0|$ *vs.* $T$ trend, namely,

(*i*) it can decrease with increasing $T$ and vanish at some $T_{\text{cross}}$ where the Gibbs functions of the state **A** and **B** intersect to each other (Fig. 6a), or,

(*ii*) it can increase with increasing $T$ starting from $T_{\text{cross}}$ (Fig. 6b).

Either situation can be now discussed assuming that $\mathrm{d}k_0/\mathrm{d}T>0$.

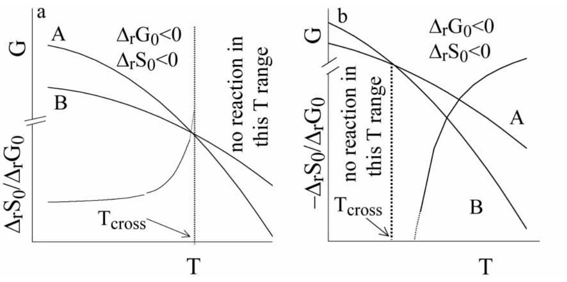

**Fig. 6** a – The process is possible for $T<T_{\text{cross}}$, b – the process is possible for $T>T_{\text{cross}}$

In the case (*i*) the driving force tends to vanish with increasing $T$, while the compliance of the medium increases and therefore counterbalances the former effect. Since at $T=T_{\mathrm{cross}}$, namely when $\Delta_r G_0$ is naught, one has

$$\left(\frac{\mathrm{d}\dot{\alpha}_0}{\mathrm{d}T}\right)_{T_{\mathrm{cross}}} = k_0 \Delta_r S_0 < 0,$$

since $\Delta_r S_0 < 0$, as the slope of the $G$(B) *vs*. $T$ trend is smaller than that of $G$(A) *vs*. $T$.

This means that a maximum of $\dot{\alpha}_0$ is expected at some $T=T_{\mathrm{max}}<T_{\mathrm{cross}}$ (which could however occur above the thermal stability threshold of the system). The maximum of $\dot{\alpha}_0$ implies that (Eq. (13))

$$\left(\frac{\mathrm{d}k_0/\mathrm{d}T}{k_0}\right)_{T_{\mathrm{max}}} = \left(\frac{\Delta_r S_0}{\Delta_r G_0}\right)_{T_{\mathrm{max}}}$$

For any $T<T_{\mathrm{max}}$, namely in the region where $(\mathrm{d}\dot{\alpha}_0/\mathrm{d}T)\geq 0$, the following condition holds:

$$\frac{\mathrm{d}k_0/\mathrm{d}T}{k_0} \geq \frac{\Delta_r S_0}{\Delta_r G_0} \tag{14}$$

Since $\Delta_r S_0<0$ and $\Delta_r G_0<0$, Eq. (14) defines the minimum positive value of $\mathrm{dlog}(k_0)/\mathrm{d}T$).

In the case (*ii*) the driving force increases with increasing $T$ with a starting threshold at $T_{\mathrm{cross}}$, below which the reaction cannot take place. Since $\mathrm{d}k_0/\mathrm{d}T>0$, $\dot{\alpha}_0$ does not go through any maximum. At $T=T_{\mathrm{cross}}$

$$\left(\frac{\mathrm{d}\dot{\alpha}_0}{\mathrm{d}T}\right)_{T_{\mathrm{cross}}} = k_0 \Delta_r S_0 > 0$$

Taking into account the expected trends of $\dot{\alpha}_0(T)$ described above and assuming that at any temperature $(\mathrm{d}\dot{\alpha}/\mathrm{d}\alpha)<0$, one can again envisage two possible pictures (Figs 7 and 8).

In either case $\dot{\alpha}(\alpha=1)=0$ at any temperature. It has to be stressed that Figs 7 and 8 correspond to ‘static’ pictures of an intrinsically dynamic reality, where any raise of $T$ produces a raise of $\alpha$. A real $\alpha=\alpha(T)$ trend can be drawn from the record of a DSC run performed at a given heating rate. The $\alpha=\alpha(T)$ trend is the projection of the reaction path $\dot{\alpha}=\dot{\alpha}[\alpha(T)]$ onto the ($\alpha$, $T$) plane (Fig. 9).

An equivalent picture can be easily drawn for $\dot{\alpha}=\dot{\alpha}[\alpha(T)]$ surface relevant to the case (*ii*).

The problem to face deals with the way to draw the kinetic law that underlies a given DSC record [10]. Once the record has been scaled with respect to the instrumental relaxation time (viz. time constant of the calorimeter used), one has to interpret the peak shaped signal.

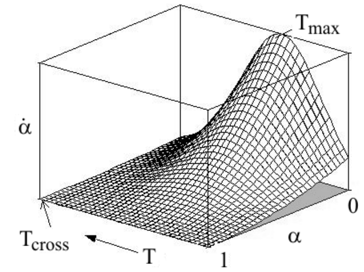

**Fig. 7** The rate $\dot{\alpha}$ increases with $T$ up to a maximum at $T_{\max}$ and then drops to zero for $T=T_{\mathrm{cross}}$

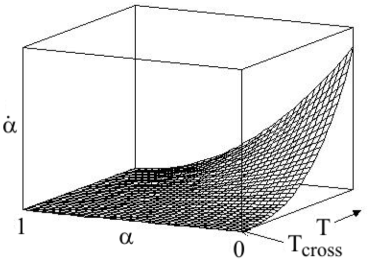

**Fig. 8** The rate $\dot{\alpha}$ increases with $T$ starting from $T=T_{\max}$ below which it is naught

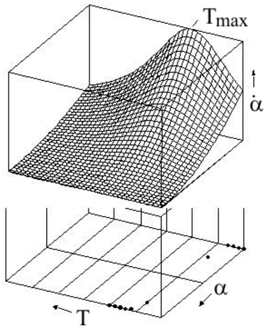

**Fig. 9** The 'static' $\dot{\alpha}=\dot{\alpha}[\alpha(T)]$ surface over the ($\alpha$, $T$) plane where the 'ideal' ($\alpha$, $T$) trend is drawn (points)

For the sake of clarity let us assume that the process may belong to the case (*ii*), viz., when $\dot{\alpha}_0$ monotonically increases with increasing $T$. It is obvious that the end of the peak corresponds to the condition $\alpha=1$, while its onset occurs at some $T\geq T_{\mathrm{cross}}$. As mentioned above, from a given DSC signal (once adjusted for base line and instrumental time lag), like the one reported in Fig. 10a, one can easily draw the $\dot{\alpha}=\dot{\alpha}[\alpha(T)]$ trend (Fig. 10b). The corresponding 3D plot is reported in Fig. 11.

From these pieces of information one can draw the function

$$\psi(T)=\frac{\dot{\alpha}(T)}{[1-\alpha(T)]}=[-\Delta_{\mathrm{r}}G_0(T)]k[\alpha(T)] \qquad (15)$$

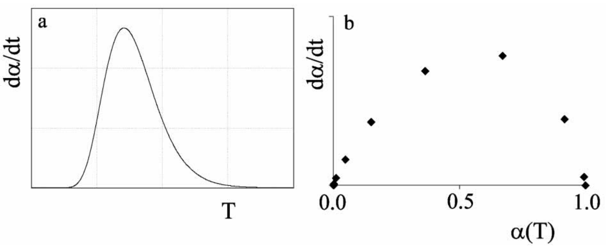

**Fig. 10** a – From the experimental DSC signal, b – one can deduce how the process rate depends on the progress degree

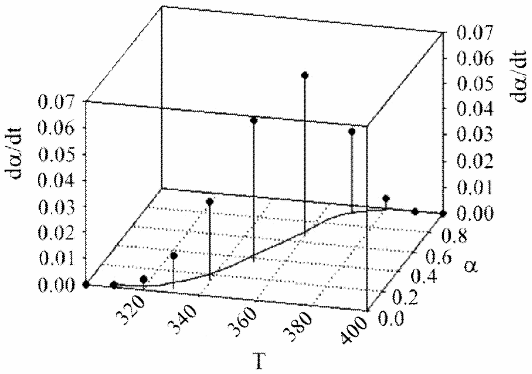

**Fig. 11** The process rate does undergo a maximum while the progress degree follows a sigmoid trend when plotted *vs*. temperature

which can be plotted *vs*. $\alpha(T)$ to recognize whether the system compliance depends on $\alpha$ (Fig. 12) or not.

In the example considered the function $\Psi(T)$ turns out to depend on $(1-\alpha)$ according to a straight line

$$\psi(T)=[-\Delta_r G_0(T)k_0(T)][1-\alpha(T)]$$

the slope of which, $[-\Delta_r G_0(T)k_0(T)]$, is 'experimentally' independent on $T$.

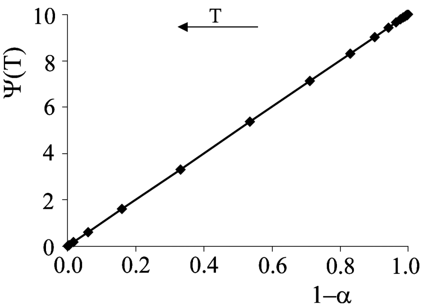

**Fig. 12** Data drawn from the DSC signal in Fig. 7 imply the function $\psi(T)$ to depend on $\alpha$

In a more complex case, one can consider the logarithm of the $\psi(T)$,

$$\ln\psi=\ln k[\alpha(T)]+\ln[-\Delta_r G_0(T)] \tag{16}$$

which can be directly drawn from the experimental data and allows a scaled view of the trend of $k[\alpha(T)]$ *vs*. $\alpha(T)$, since $\Delta_r G_0(T)$, although not estimated, does not depend on $\alpha$.

Once again one can consider starch gelatinization as a suitable example of a complex process that produces a DSC signal which cannot be explained without accounting for the change of the system compliance. It was so far recognized that even when the relevant DSC signal appeared as a well shaped endothermic peak, as in the case of potato starch in excess water [12], the relevant kinetic parameterization did not obey a simple kinetic law and, above all, it did not follow an Arrhenius-like behaviour. The same occurs in a more complex situation [13], namely, starch gelatinization in a wheat flour dough (with about 50% water mass content). Figure 13a reports the whole DSC trace obtained at 5°C $\min^{-1}$ heating rate. The signal, deconvoluted into gaussian components [13], reveals that the starch gelatinization corresponds to the first two gaussian components, the others being related to decomposition of amylose/lipid complexes. When the contribution relevant to the starch gelatinization is singled out, the corresponding trace is that reported in Fig. 13b and the progress of the transition $\alpha$, determined as the fraction of the underlying area, is given in Fig. 14a. These data allows evaluation of the function $\Psi$, which shows a behaviour (Fig. 14b) much more complex than that reported in Fig. 12.

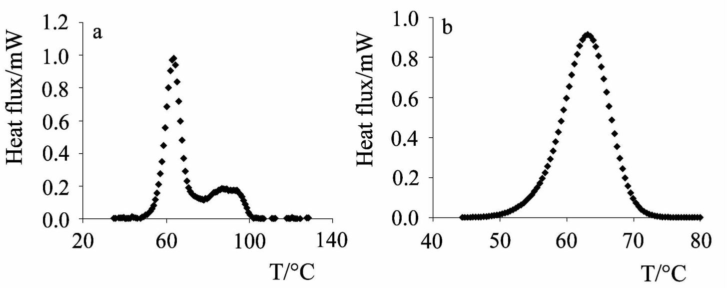

**Fig. 13** Starch gelatinization in a wheat flour doguh. a – the overall DSC record trace, b – the signal relevant to starch gelatinization singled out from the overall record through deconvolution into four gaussian functions [13]

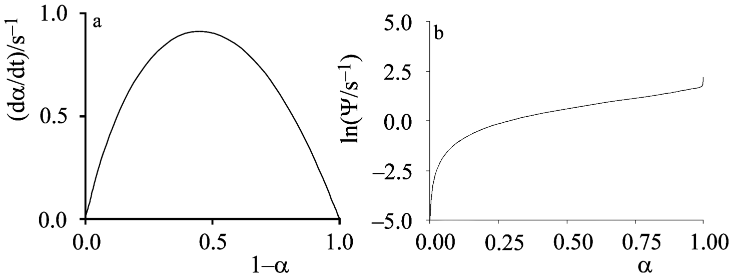

**Fig. 14** a – Rate of starch gelatinization in a wheat flour dough drawn from the relevant DSC record, b – calculated trend of the $\psi$ function (see text) that reflects the change of the medium compliance in the course of the transition

## Conclusions

When the process rate is treated as the result of the effects of a thermodynamic driving force, identified with the residual drop of the Gibbs function at every elapsed time, and of the medium compliance (or hindrance), expressions can be drawn which are rather similar to those of the classical chemical kinetics in the gas phase and dilute solutions, but imply some physical meaning of the relevant parameters, namely, kinetic constant and kinetic order. Multistep processes, like consecutive and enzymatic reactions, can be accordingly treated.

The first consequence of this approach is that both the apparent kinetic constant and kinetic order are related to the driving force and the medium compliance. In particular, the contribution of the driving force to the overall kinetic order is always equal to one, while that of the medium compliance can be separately evaluated from experimental data and can change with the progress of the reaction.

The effects of temperature changes are formally expressed, although in a still largely implicit form which cannot be oversimplified in the form of the traditional Arrhenius expression.

DSC (and other suitable thermal analysis) records can provide experimental data in a form that is very adequate to compute and draw the trends of the driving force and the medium compliance during the progress of the reaction in non isothermal conditions.

As for DSC and IC investigations, the approach proposed allows evidence of concurrent events which may have negligible thermal effects and therefore do not significantly modify the overall enthalpic balance of a given process, although can dramatically affect its rate either in isothermic or in non isothermic conditions.

## Appendix

*Multistep processes*

Many processes of practical interest, like consecutive and enzymatic reactions, imply some intermediate step between starting and ending state, viz.,

$$A \xrightarrow{1} B \xrightarrow{2} C \qquad \text{(A1)}$$

$$A \underset{-1}{\overset{1}{\leftrightarrows}} B \xrightarrow{2} C \qquad \text{(A2)}$$

These cases can be formally described through the same approach presented above by replacing the progress degree of each step with some mass fractions. For the sake of simplicity molar fractions are used in the expressions reported below.

$$f_A = N_A/(N_A+N_B+N_C),$$

$N_i$ standing for number of moles of component '*i*' ($i$=A, B, C), which obey the condition that

$$f_A+f_B+f_C=1$$

In the case of simple consecutive reactions (Eq. (A1)), the step 1 implies a drop of the Gibbs function that can be written as:

$$\begin{aligned}\Delta_r G_1 &= G_B - f'_B G_B - f'_A G_A = (1-f_B)(G_B-G_A)= \\ &=(1-f'_B)\Delta_r G_{1,0}=f'_A\Delta_r G_{1,0}\end{aligned} \tag{A3}$$

where $f'_B=N_B/(N_B+N_A)$ is a pseudomolar fraction that replaces the progress degree of step 1. An analogous expression can be written for step 2:

$$\begin{aligned}\Delta_r G_2 &= G_C - f''_C G_C - f''_B G_B = (1-f''_C)(G_C-G_B)= \\ &=(1-f''_C)\Delta_r G_{2,0}=f''_B\Delta_r G_{2,0}\end{aligned} \tag{A4}$$

The rate of step 1 can be defined as $\dot{f}'_A$ (time derivative of $f'_A$),

$$\dot{f}'_A=-\Delta_r G_{1,0}k_1 f'_A=\chi_1 f'_A=\frac{\dot{f}_A(f_A+f_B)-f_A(\dot{f}_A+\dot{f}_B)}{(f_A+f_B)^2} \tag{A5}$$

where $\chi_1=-(k_1\Delta_r G_{1,0})<0$, from which,

$$\dot{f}_A=\frac{\chi_1 f_A+f'_A\dot{f}_B}{f'_B} \tag{A6}$$

From the expression for the rate of step 2, $\dot{f}''_C$, where $\chi_2=-(k_2\Delta_r G_{2,ø})<0$, one can draw

$$\dot{f}_C=\frac{f''_C\dot{f}_B-\chi_2 f_B}{f''_B} \tag{A7}$$

Taking into account that $\dot{f}_B=-(\dot{f}_A+\dot{f}_C)$, one can finally obtain:

$$\begin{aligned}\dot{f}_A &= \frac{f_A(1-f_A)}{f_B}[\chi_1(f_A+f_B)+\chi_2 f_B] \\ \dot{f}_B &= \chi_2 f_B(1-f_A)-\chi_1(f_A+f_B) \\ \dot{f}_C &= -\frac{(f_A+f_B)}{f_B}[\chi_2 f_B(1-f_A)+\chi_1 f_A f_C]\end{aligned} \tag{A8}$$

The second expression in Eq. (A8) shows that $f_B$ goes through a maximum as expected.

When the first step corresponds to a couple of opposite reactions (Eq. (A2)), as in simple enzymatic processes, with apparent kinetic constant $\chi_1$ and $\chi_{-1}$, one can easily obtain that:

$$\begin{aligned}\dot{f}_A &= [\chi_1 f_A - \chi_{-1} f_B] + \chi_2 f_A (1-f_A)\\ \dot{f}_B &= \chi_2 f_B (1-f_A) - [\chi_1 f_A - \chi_{-1} f_B](f_A+f_B)\\ \dot{f}_C &= -f_C[\chi_1 f_A - \chi_{-1} f_B] - \chi_2 (f_A+f_B)(1-f_A)\end{aligned} \tag{A9}$$

Equations (A8) and (A9) hold for any apparent kinetic order of each step involved since the relevant apparent kinetic constants, $\chi_1$, $\chi_{-1}$, and $\chi_2$, do depend on both temperature and composition. They can be used to work out the experimental values of the three molar fractions and related change rates which can be described with suitable continuous functions of the time. Replacing such values (or fitting functions) within Eqs (A8) and/or (A9) one can draw the corresponding trends of the apparent kinetic constants *vs.* the time and therefore *vs.* the composition of the system. Finally, by use of Eq. (16) the relevant $\Delta_r G_o$ and $k_j = k_j(f_i)$ can be singled out.

## References

1 H. Eyring and E. M. Eyring, Modern Chemical Kinetics, Van Nostrand Reinhold, London 1963.

2 F. Lindemann, see discussion reported in K. J. Laidler, Chemical Kinetics, Harper and Row Publ., 1987.

3 E. Santacesaria, Catalysis Today, 52 (1999) 113.

4 S. Wang and H. Hofmann, Chem. Eng. Sci., 54 (1999) 1639.

5 S. Toxvaerd, Comp. Phys. Comm., 121–122 (1999) 251.

6 J. Sempere, R. Nomen and R. Serra, J. Therm. Anal. Cal., 56 (1999) 843 and therein quoted previous works by the same Authors.

7 J. Šesták and Z. Chvoj, 2001, private communication to be submitted for publication.

8 G. Nicolis, Rep. Progr. Phys., 42 (1979) 225.

9 D. K. Kondepudi and I. Prigogine, Modern Thermodynamics: from Heat Engines to Dissipative Processes, Wiley, London 1998.

10 A. Schiraldi, L. Piazza, D. Fessas and M. Riva, in Handbook of Thermal Analysis and Calorimetry, Vol. 4, From Macromolecules to Man, R. B. Kemp Ed., Elsevier Publ., Amsterdam 1999, pp. 829–921, see appendix of the paper.

11 M. Riva, A. Schiraldi and L. Piazza, Thermochim. Acta, 246 (1994) 317.

12 M. Riva and A. Schiraldi, Thermochim. Acta, 220 (1993) 117.

13 D. Fessas and A. Schiraldi, J. Therm. Anal. Cal., 61 (2000) 411.