

# Chapter 1

## Some Basics En Route to Isoconversional Methodology

### 1.1 From Condensed-Phase Kinetics to Isoconversional Principle

*Following, then, the order of nature, let us begin with the principles which come first.*

Aristotle, Poetics.

This book deals with kinetics of thermally stimulated processes. Kinetics studies the rates of processes in order to accomplish two major objectives. The first is to parameterize the process rate as a function of state variables so that it can be predicted for any combination of these variables. The second is to obtain insights into the process mechanisms. Thermally stimulated processes are the processes that can be initiated by changes in temperature or, in other words, by heating or cooling. More specifically, we are concerned with the thermally stimulated processes that take place in the condensed-phase systems, i.e., liquids and solids.

A change in temperature directly affects all types of molecular motion in the system causing physical and chemical processes inside it. The energy of the molecular motion increases with increasing temperature. When the energy of the molecular motion approaches the energy of intermolecular interactions, the cohesive forces can no longer hold the molecules in the condensed phase so that the latter transforms into the gas phase. As a result, a liquid vaporizes and a solid sublimates. These are examples of a physical process, i.e., a process that does not break the bonds within the molecules. On the other hand, physical processes can also be stimulated by a decrease in temperature. As the energy of the molecular motion drops, the state of the system becomes increasingly determined by the intermolecular interactions that may cause the formation of various structures. Examples of such physical processes are crystallization of a melt or gelation of a solution.

However, when the temperature is raised sufficiently high, the energy of the molecular motion begins approaching the energy of chemical bonds so that the latter break and cause the system to undergo chemical transformations. Thermal decom-

position of a solid substance and thermal polymerization of a liquid monomer are examples of a chemical process.

A change in temperature not only stimulates a variety of physical and chemical processes but also affects their kinetics. There are many experimental techniques that can be used for measuring the kinetics of thermally stimulated processes as a function of temperature. Although the applications of the kinetic methodology discussed in this book are not limited to any particular experimental techniques, all kinetic results collected here have been obtained by either differential scanning calorimetry (DSC) or thermogravimetric analysis (TGA). Other applications include mass spectrometry [1, 2], infrared spectroscopy [3, 4], dilatometry [5], rheometry [6], thermomechanical, dynamic mechanical analysis [3, 7], and acoustic measurements [8].

DSC and TGA are the most common techniques falling under the umbrella of thermal analysis. Detailed information on the techniques and their applications is available elsewhere [9–11]. Briefly, TGA measures changes in the sample mass that makes it suitable for monitoring the kinetics of mass loss in such processes as vaporization, sublimation, decomposition, or of mass gain in oxidation. DSC measures the heat flow either from or to the sample. Since practically any process generates detectable heat flow, DSC has an extremely broad application range. However, it is most commonly employed to measure the kinetics of processes that occur without any mass change such as crystallization, melting, gelation, and polymerization. Either technique, TGA or DSC, is capable of conducting measurements under precisely controlled temperature conditions that can be isothermal or nonisothermal. The latter typically means heating or cooling at a constant rate of temperature change.

The rate of many thermally stimulated processes can be parameterized in terms of  $T$  and  $\alpha$  as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha), \quad (1.1)$$

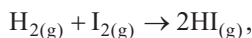
where  $t$  is the time,  $T$  is the temperature,  $\alpha$  is the extent of conversion,  $f(\alpha)$  is the reaction model, and  $k(T)$  is the rate constant. The latter is almost universally represented by the Arrhenius equation:

$$k(T) = A \exp\left(\frac{-E}{RT}\right), \quad (1.2)$$

where  $A$  is the preexponential factor,  $E$  is the activation energy, and  $R$  is the gas constant. Equation 1.1 is quite different from the basic rate equation found in textbooks dealing with homogeneous reactions in gases and solutions [12]:

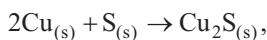
$$-\frac{dC}{dt} = k(T)C^n, \quad (1.3)$$

where  $C$  is the concentration and  $n$  is the reaction order. For a reaction to be homogeneous, the reactants should be miscible at the molecular level and be present in the form of single phase. Then, the reaction would occur throughout the whole reaction volume and its rate would be proportional to the amount of reactants in this volume or, in other words, to their concentrations. For instance, in a gas-phase reaction:



the two gases are mixed in a reaction vessel and the reaction zone is the whole volume of the vessel. Increasing the amounts of gases in the reaction vessel increases the number molecules in the reaction zone and, thus, the reaction rate.

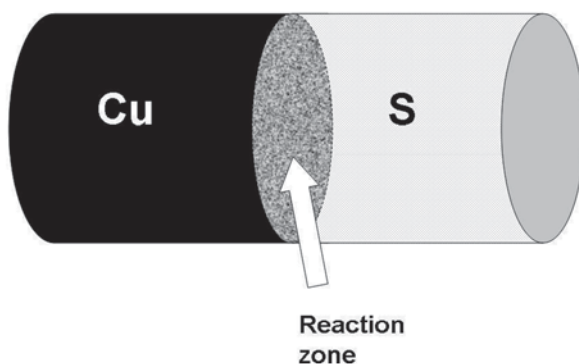
However, this does not hold if the reactants cannot be mixed at the molecular level and thus have to be present as individual phases. Such reactions can occur only at the interface of the reactant phases. The reactions of this type are called heterogeneous. For example, in a reaction:



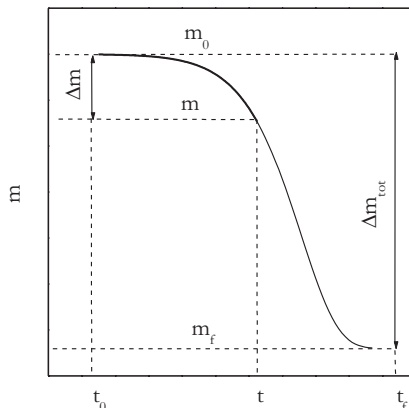
two solid reactants are brought into a contact so that the reaction zone is limited to the interfacial contact area. If the copper and sulfur reactants are prepared in the form of cylinders (Fig. 1.1) with the circular bases of equal size and made to react by bringing the bases of the solid cylinders into a contact, the reaction rate will be proportional to the area of the circular bases. Nevertheless, it will be independent of the total amount of copper and sulfur outside the interfacial reaction zone, i.e., independent of the cylinder heights. For this reason, the total amounts of the reactants that can be expressed as the concentration do not carry much meaning for heterogeneous kinetics.

Note that the processes that include a condensed phase generally tend to demonstrate heterogeneous kinetics. Reactions between solids, or solids and liquids,

**Fig. 1.1** Schematic representation of a reaction between two solids,  $\text{Cu}(s)$  and  $\text{S}(s)$



**Fig. 1.2** Evaluation of conversion from TGA curve



or two immiscible liquids, decomposition of solids to gases, reaction of gases with solids and liquids, dissolution of solids, evaporation of liquids, sublimation, and melting of solids are all examples of processes whose kinetics is heterogeneous. Considering that for the heterogeneous kinetics the only concentration that matters is the concentration of the reactants in the interfacial reaction zone and that this concentration is not readily measurable, it is only practical to switch from the concentration to the extent of the reactant conversion ( $\alpha$ ). This parameter simply reflects the reaction progress from the initial state, i.e., before the reaction starts ( $\alpha=0$ ) to the final state, i.e., when the reaction is complete ( $\alpha=1$ ).

The conversion is readily determined as a fractional change of any physical property associated with the reaction progress. When the process progress is monitored as a change in mass by TGA,  $\alpha$  is determined as a ratio of the current mass change,  $\Delta m$ , to the total mass change,  $\Delta m_{tot}$  occurred throughout the process:

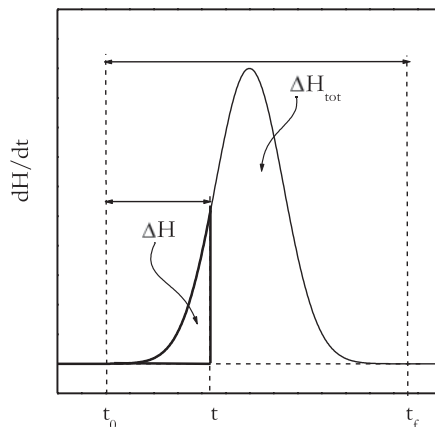
$$\alpha = \frac{m_0 - m}{m_0 - m_f} = \frac{\Delta m}{\Delta m_{tot}}, \quad (1.4)$$

where  $m_0$  and  $m_f$ , respectively, are the initial and final masses (Fig. 1.2). In its turn, when the progress is measured as a change in heat by DSC,  $\alpha$  is evaluated as a ratio of the current heat change,  $\Delta H$ , to the total heat released or absorbed,  $\Delta H_{tot}$  in the process:

$$\alpha = \frac{\int_{t_0}^t (dH / dt) dt}{\int_{t_0}^{t_f} (dH / dt) dt} = \frac{\Delta H}{\Delta H_{tot}}, \quad (1.5)$$

where  $dH/dt$  is the heat flow measured by DSC (Fig. 1.3).

**Fig. 1.3** Evaluation of conversion from DSC curve



Similarly, if the concentration of a reactant is available, it can easily be converted to the conversion. For example, if the value of  $C$  varies throughout the reaction from the initial value  $C_0$  to zero, the conversion is:

$$\alpha = \frac{C_0 - C}{C_0}. \quad (1.6)$$

Isolating  $C$  from Eq. 1.6 and substituting the resulting expression into Eq. 1.3 leads to:

$$\frac{d\alpha}{dt} = k'(T)(1 - \alpha)^n, \quad (1.7)$$

where  $k'(T) = C_0^{n-1}k(T)$ . Equation 1.7 is the basic equation of homogeneous kinetics. Comparing it against Eq. 1.1 suggests that homogeneous kinetics can be described by a simple reaction model:

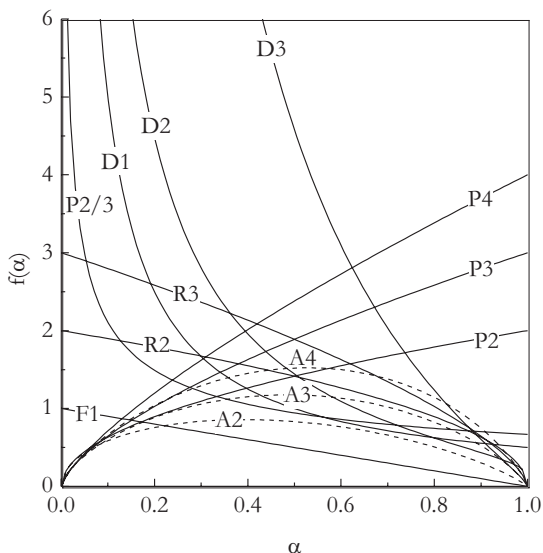
$$f(\alpha) = (1 - \alpha)^n. \quad (1.8)$$

that is called a reaction-order model.

Fitting the rate to the reaction models may provide some clues about the reaction mechanism. Fitting homogeneous kinetics data to a reaction-order model (Eq. 1.8) and determining that  $n$  equals 1 or 2 suggests that the reaction is, respectively, monomolecular or bimolecular. In heterogeneous kinetics, the situation is not nearly as simple. There are dozens of heterogeneous reaction models that have been derived under various mechanistic assumptions [9, 13]. Such multitude of the models arises from the need to describe the multitude of ways by which the spatially localized reaction zone propagates throughout the reactants. The mathematical equations and names of some models are collected in Table 1.1. Figure 1.4 displays the model dependencies of  $f(\alpha)$  on  $\alpha$ .

**Table 1.1** Some kinetic models used in the heterogeneous kinetics

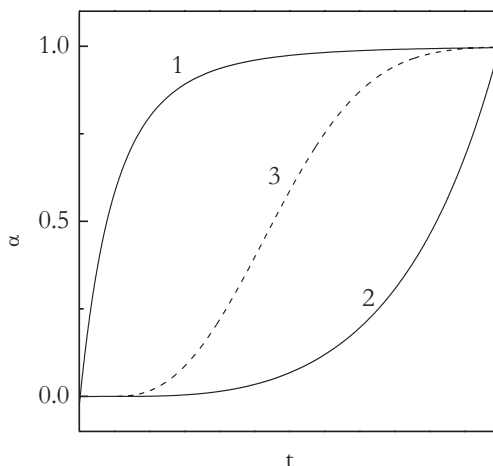
	Reaction model	Code	$f(\alpha)$	$g(\alpha)$
1	Power law	P4	$4\alpha^{3/4}$	$\alpha^{1/4}$
2	Power law	P3	$3\alpha^{2/3}$	$\alpha^{1/3}$
3	Power law	P2	$2\alpha^{1/2}$	$\alpha^{1/2}$
4	Power law	P2/3	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
5	One-dimensional diffusion	D1	$1/2\alpha^{-1}$	$\alpha^2$
6	Mampel (first order)	F1	$1-\alpha$	$-\ln(1-\alpha)$
7	Avrami–Erofeev	A4	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	$[- \ln(1-\alpha)]^{1/4}$
8	Avrami–Erofeev	A3	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$
9	Avrami–Erofeev	A2	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
10	Three-dimensional diffusion	D3	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
11	Contracting sphere	R3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
12	Contracting cylinder	R2	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
13	Two-dimensional diffusion	D2	$[- \ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$

**Fig. 1.4** The  $f(\alpha)$  on  $\alpha$  dependencies for the reaction models from Table 1.1

Since under the isothermal conditions (i.e.,  $T = \text{const}$ )  $k(T)$  is constant, the rate is directly proportional to  $f(\alpha)$ :

$$\frac{d\alpha}{dt} = \text{Const} \cdot f(\alpha). \quad (1.9)$$

**Fig. 1.5** Three major types of integral kinetic curves obtained under isothermal conditions: 1 decelerating; 2 accelerating; 3 autocatalytic (sigmoid)



Then from the  $f(\alpha)$  dependencies presented in Fig. 1.4, we can identify three major types of heterogeneous kinetics: decelerating, accelerating, and autocatalytic. For the decelerating kinetics, the rate is continuously decreasing as the process progresses from  $\alpha=0$  to 1. This type of behavior is represented by the diffusion models and the models of contracting geometry. This is also the typical behavior for the homogeneous kinetics that obey the reaction-order model (Eq. 1.8). For the accelerating kinetics, the rate is constantly increasing throughout the process progress. The power law models provide an example of such behavior. The autocatalytic models describe processes whose rate passes through a maximum. The Avrami–Erofeev models of nucleation and growth are typical representatives of such kinetic behavior.

The three types of heterogeneous kinetics are also easy to recognize from the integral kinetic curves,  $\alpha$  versus  $t$ , obtained under isothermal conditions (Fig. 1.5). The decelerating kinetic curves are almost linear in the initial portion but start to bend at larger extents of conversion and ultimately reach a plateau as  $\alpha$  approaches 1. The accelerating and autocatalytic kinetic curves demonstrate little change at the lowest extents of conversion, sometimes featuring a distinct plateau. The latter is also called an induction period. Past this period, the curves start to bend at a continuously increasing angle. In the accelerating curves, this trend persists until completion, i.e.,  $\alpha=1$ . In the autocatalytic curves, acceleration switches to deceleration at some intermediate extent of conversion. This gives rise to the characteristic sigmoid shape of the curves. The respective reaction models and kinetics are sometimes referred to as sigmoid.

Speaking of identifying particular reaction models (Fig. 1.4) rather than the types of kinetics (Fig. 1.5), a quick review of Fig. 1.4 immediately reveals that many of the models do not show a significant difference especially in certain ranges of  $\alpha$ . Considering that all models largely oversimplify the reality, experimental data tend not to follow the models accurately. It is frequently found that experimental data fall between two model dependencies, or coincide with one model at smaller

conversions but with another at larger ones, or do not follow any model within a certain range conversions. This creates a serious problem of identifying the reaction models by means of the model-fitting procedure.

The problem of identifying the reaction models becomes practically insurmountable when model fitting is performed on experimental data obtained in a nonisothermal run at a single heating rate,  $\beta$ . Note that under isothermal conditions the conversion dependence of the reaction rate (i.e., an experimental dependence of  $f(\alpha)$  on  $\alpha$ ) is easy to isolate because the rate is directly proportional to  $f(\alpha)$  (see Eq. 1.9). However, under nonisothermal conditions when the temperature changes linearly with the time:

$$\beta = \frac{dT}{dt}, \quad (1.10)$$

both  $\alpha$  and  $T$  change simultaneously that thwarts clean separation of  $f(\alpha)$  and  $k(T)$  in Eq. 1.1. That is, when Eq. 1.1 is fitted to nonisothermal data, any inaccuracy in selecting the reaction model becomes compensated by the respective inaccuracy in the rate constant. As a result of this compensation, there always is more than one set of  $k(T)$  and  $f(\alpha)$  that can fit the experimental data equally well from the statistical point of view [14]. The resulting different rate constants give rise to widely differing pairs of the Arrhenius parameters,  $E$  and  $A$ , which, however, are strongly correlated via the so-called compensation effect [15]:

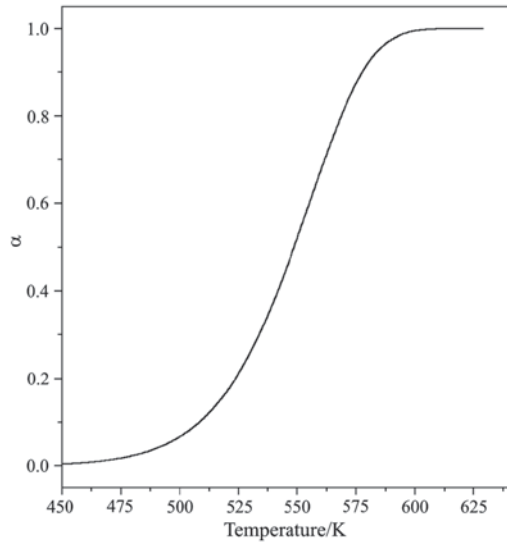
$$\ln A_j = aE_j + b, \quad (1.11)$$

where the subscript  $j$  denotes a particular reaction model  $f_j(\alpha)$  that is used in the model-fitting procedure. A set of  $f_j(\alpha)$ ,  $E_j$ , and  $A_j$  is frequently called a kinetic triplet. Experimental examples of the problem have been considered by Vyazovkin and Wight [14]. Instructive simulated examples are found in the papers by Criado et al. [16, 17], who have demonstrated that three different kinetic triplets can give rise to exactly the same kinetic curve  $\alpha$  versus  $T$  (Fig. 1.6). Note that the respective Arrhenius parameters are strongly correlated via the compensation effect (Fig. 1.7).

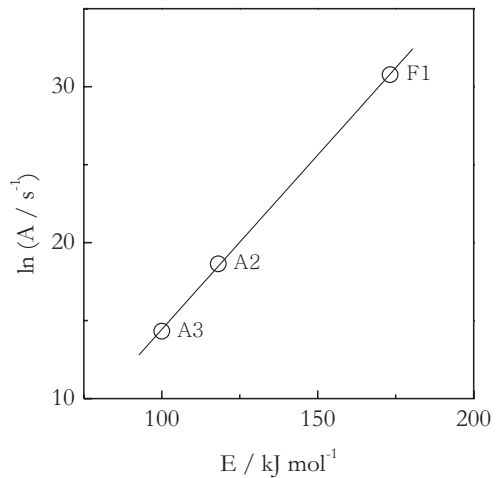
Although the deficiency of single-heating-rate kinetic analyses had been emphasized repeatedly, their general inability to produce reliable kinetic triplets was officially recognized by the community only in the discussions [18–21] of the results of the 2000 Kinetic Project sponsored by the International Confederation of Thermal Analysis and Calorimetry (ICTAC). One of the most important conclusions of that project was that the single-heating-rate kinetic analyses should be avoided. As an alternative, one should use kinetic analyses based on the simultaneous use of multiple heating rates or, more, generally, multiple temperature programs. According to the 2011 recommendations [22] of the ICTAC Kinetics Committee, such kinetic analyses should be performed by using either model-fitting or isoconversional (model-free) kinetic methodologies. The use of the model-fitting methodology is outside this book's scope. The book focuses entirely on the applications of the isoconversional kinetic methodology or, simply, isoconversional kinetics.



**Fig. 1.6** The same kinetic curve can be represented by three different triplets (F1:  $E=172.3 \text{ kJ mol}^{-1}$ ,  $A=2.30 \times 10^{13} \text{ s}^{-1}$ ; A2:  $E=118.1 \text{ kJ mol}^{-1}$ ,  $A=1.24 \times 10^8 \text{ s}^{-1}$ ; A3:  $E=100.0 \text{ kJ mol}^{-1}$ ,  $A=1.66 \times 10^6 \text{ s}^{-1}$ ; heating rate is  $1^\circ\text{C min}^{-1}$ ). (Reproduced from Criado et al. [17] with permission of Springer)



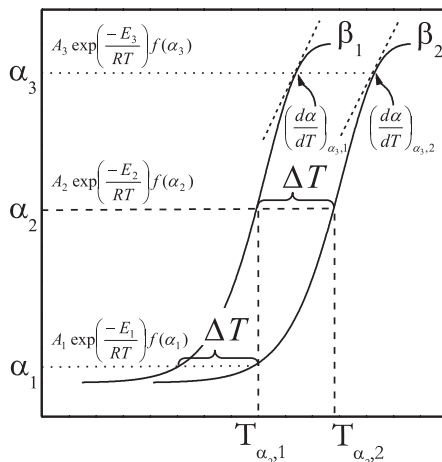
**Fig. 1.7** Arrhenius parameters related to the kinetic curve in Fig. 1.6 obey the compensation effect:  $\ln A = aE + b$



The isoconversional kinetics takes its origin in the isoconversional principle that allows one to eliminate the reaction model from kinetic computations. The principle states that the process rate at constant extent of conversion is only a function of temperature. This is easy to derive from Eq. 1.1 by taking the logarithmic derivative of the rate at  $\alpha = \text{const}$ :

$$\left[ \frac{\partial \ln(d\alpha / dt)}{\partial T^{-1}} \right]_{\alpha} = \left[ \frac{\partial \ln k(T)}{\partial T^{-1}} \right]_{\alpha} + \left[ \frac{\partial \ln f(\alpha)}{\partial T^{-1}} \right]_{\alpha}, \quad (1.12)$$

**Fig. 1.8** Isoconversional method uses an individual rate equation for each extent conversion and a narrow temperature interval  $\Delta T$ , related to this conversion. The use of different heating rates,  $\beta_1$  and  $\beta_2$ , allows for determining different rates  $\left(\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT}\right)$  at the same conversion. (Reproduced from Vyazovkin and Sbirrazzuoli [23] with permission of Wiley)



where the subscript  $\alpha$  indicates isoconversional values, i.e., the values related to a given extent of conversion. The second addend on the right-hand side of Eq. 1.12 is zero because at  $\alpha = \text{const}$ ,  $f(\alpha)$  is constant. The first addend readily derives from Eq. 1.2 so that Eq. 1.12 reduces to:

$$\left[ \frac{\partial \ln(d\alpha / dt)}{\partial T^{-1}} \right]_{\alpha} = -\frac{E_{\alpha}}{R}. \quad (1.13)$$

It follows from Eq. 1.13 that the temperature dependence of the isoconversional rate can be utilized to determine the isoconversional values of the activation energy,  $E_{\alpha}$  without identifying or assuming any form of the reaction model. That is why isoconversional methods are frequently termed as “model-free” methods. While catchy, this term is not to be taken literally. It should be kept in mind that although the methods do not have to identify explicitly the model, they still assume implicitly that there is some  $f(\alpha)$  that defines the conversion dependence of the process rate.

The temperature dependence of the isoconversional rate is obtained experimentally by performing a series of runs at different temperature programs. It usually takes four to five runs at different heating rates or at different temperatures to determine such dependence. Figure 1.8 [23] illustrates the idea of determining the isoconversional rate from two nonisothermal runs conducted at the heating rates  $\beta_1$  and  $\beta_2$ . The conversion versus temperature plots can be estimated by scaling TGA data in accord with Eq. 1.4 (Fig. 1.2). By selecting a certain conversion  $\alpha$ , one then finds the temperature related to it at each heating rate, i.e.,  $T_{\alpha,1}$  and  $T_{\alpha,2}$ . The conversions need to be selected in a wide  $\alpha$  range, e.g., 0.05–0.95 with a step not larger than 0.05. Since it is unlikely that the experimental  $\alpha$  versus  $T$  curves would contain points exactly at selected values of  $\alpha$  one has to use interpolation to find the values of  $T_{\alpha}$ . Then the slope (numerical derivative) of the  $\alpha$  versus  $T$  curve at  $T_{\alpha}$  would give the values of  $\left(\frac{d\alpha}{dT}\right)_{\alpha}$  that can be converted to the isoconversional rate as follows:

$$\left(\frac{d\alpha}{dt}\right)_{\alpha} = \left(\frac{d\alpha}{dT}\right)_{\alpha} \beta. \quad (1.14)$$

Equation 1.14 is derived by substitution of the derivatives in accord with Eq. 1.9. The isoconversional rates are also obtainable from DSC data that would have to be converted to  $\alpha$  versus  $T$  curves (Eq. 1.5, Fig. 1.3) to estimate the values of  $T_{\alpha}$ . The isoconversional rate is then estimated from the experimentally measured flow rate at  $T_{\alpha}$  as follows:

$$\left(\frac{d\alpha}{dt}\right)_{\alpha} = \frac{1}{\Delta H_{\text{tot}}} \left(\frac{dH}{dt}\right)_{T_{\alpha}}. \quad (1.15)$$

Once the temperature dependence of the isoconversional rate is determined from a series of temperature programs, e.g., several heating rates or several temperatures, it can be parameterized through a combination of Eqs. 1.1 and 1.2 as:

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln[A_{\alpha}f(\alpha)] - \frac{E_{\alpha}}{RT_{\alpha,i}}, \quad (1.16)$$

where the subscript  $i$  represents the number of the temperature program. This equation is the base of the differential isoconversional method by Friedman [24]. A plot on the left-hand side of Eq. 1.16 against the reciprocal temperature gives a straight line whose slope yields the isoconversional value of the effective activation energy,  $E_{\alpha}$ , without any assumptions about the process model. The two other parameters of the kinetic triplet (preexponent and reaction model) are encrypted in the intercept but they can be evaluated by using several simple techniques discussed in Chap. 2.

Repeating the calculations (Eq. 1.16) for every value of  $\alpha$  results in evaluating a dependence of the effective activation energy on the extent of conversion. Obtaining such dependence is the major outcome of the application of the Friedman method as well as of any other isoconversional method. An overview of the methods is provided in Chap. 2. For now, we need to point out the effective nature of the activation energy estimated. The term “effective” as well as “overall,” or “global,” or “apparent” is used to emphasize that the activation energy estimated from experimental kinetic data does not necessarily have a simple meaning signified by Eq. 1.1. This equation is an equation of a single-step process that means that all the reactants become converted to the products by overcoming the same energy barrier,  $E$ . As discussed later, single-step pathways in condensed-phase and heterogeneous kinetics are rather an exception than a rule. The application of the single-step equation to a process whose rate may be determined by more than one step results in estimating an activation energy that may be linked to more than one energy barrier. For this reason, experimentally determined activation energy generally provides information on an averaged or effective energy barrier that is the barrier that corresponds to the actual temperature dependence of the experimentally measured process rate. It

should be noted that experimental estimates of the preexponential factor and reaction model are also generally effective in their nature.

This book discusses amply how the  $E_\alpha$  versus  $\alpha$  dependencies can be estimated and employed for obtaining mechanistic insights, making kinetic predictions, and estimating the two other members of the kinetic triplet. All these actions comprise the body of isoconversional kinetic analysis. The first thing one learns from this analysis is whether the effective activation energy varies with conversion. If  $E_\alpha$  does not demonstrate any significant variation with  $\alpha$ , the process can be described by a single effective activation energy. This does not necessarily mean that the process in question is a single-step process. More likely, it is a multistep process that has one step whose rate determines the overall process rate. It may also be that the steps that dominate the overall kinetics have insignificantly different activation energies.

When  $E_\alpha$  is found to vary significantly with  $\alpha$ , the process is likely to involve two or more steps having differing activation energies. Under this circumstance, a single-step rate equation (Eq. 1.1) cannot be applied to describe the process kinetics in the whole range of experimental conversions and temperatures. Nevertheless, the occurrence of a multistep process should not be taken as immediate invalidation of the isoconversional principle, notwithstanding the latter holds strictly for a single-step process. The principle still works as a fair approximation because isoconversional methods describe the process kinetics by using multiple single-step kinetic equations, each of which represents only a single extent of conversion and a narrow temperature range ( $\Delta T$ ) associated with it (Fig. 1.8).

Multistep model fitting is sometimes suggested as a better alternative to isoconversional kinetic analysis. In the ideal case when the number of steps and interrelationship between them (i.e., the mechanism) are known, the multistep model fitting would certainly secure the best possible solution. In reality, most of the time one has to deal with the processes whose mechanism is unknown. In this situation, the number of steps and the mechanism that comprises them have to be guessed and tested by statistical criteria of the fits. It is not uncommon when multistep model fitting cannot differentiate statistically between alternative mechanisms, e.g., parallel and consecutive reactions [18, 20]. For any particular mechanism, the number of steps is usually determined by increasing it consecutively until the introduction of a new step does not result in statistically significant improvement of the fit.

Even if statistical analysis allows one to select a particular mechanism and the number of steps with fair certainty, it does not mean that the resulting multistep model is an accurate representation of the actual process. It should always be kept in mind that statistics evaluates the models only by the quality of the data fit but not by the physical sense of applying the models to the data. The best fit can be easily accomplished by an equation devoid of any physical meaning [25]. This is not to say that multistep model fitting is inferior to isoconversional kinetic analysis. Rather, each approach has its limitations and inaccuracies. An isoconversional method approximates multistep kinetics by a sequence of independent single-step equations, none of which is an accurate representation of the actual multistep kinetics. Multistep fitting approximates multistep kinetics by an interrelated combination of single-step equations, in which the number and interrelationship of the steps do

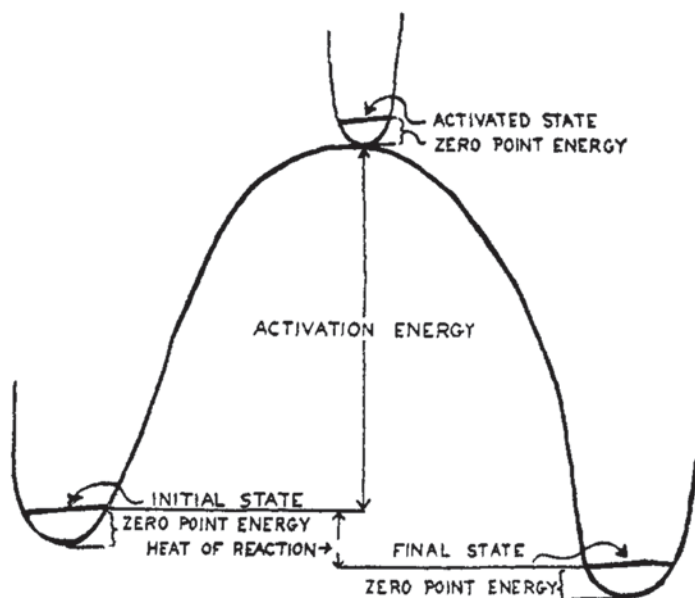
not represent accurately the actual multistep kinetics. In either case, the result of analysis is a set of kinetic triplets that are effective because the actual kinetics gets averaged through the use of approximate models. At any rate, when dealing with condensed-phase and heterogeneous kinetics one needs to understand the meaning of effective kinetic parameters. Applied to isoconversional methods, this means to understand the concept of variable activation energy.

## 1.2 Understanding Variable Activation Energy

*Then I wanted to know the meaning of the fourth beast, which was different from all the others and most terrifying.*

Daniel 7:19

Variable activation energy (i.e., the activation energy that varies with temperature and/or conversion) would be much easier to appreciate, if it were not for that eye-catching graph found in undergraduate general or physical chemistry texts in sections dealing with kinetics or, more specifically, with the activated-complex theory. An example of such graph is shown in Fig. 1.9 borrowed from a classical paper by Eyring [26]. This graph perfectly captures the essence of a reaction act, in which reactants must overcome some energy barrier in order to turn into products. The graph is so self-explanatory and the idea appears so straightforward that the constancy



**Fig. 1.9** Energy barrier in the theory of the activated complex. (Reproduced from Eyring [26] with permission ACS)

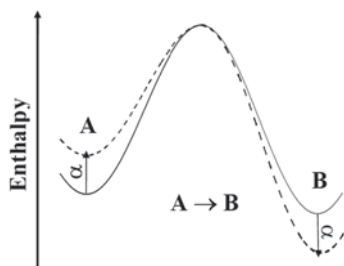
of the energy barrier as well as of the activation energy representing this barrier does not raise much of a doubt. Nonetheless, the situation presented in this graph is grossly oversimplified. It represents a reaction between two reactant molecules that get converted to two product molecules. That is, there is no reaction medium, in which the energies of the molecules, engaged in the reaction act, would be affected by intermolecular interactions with surrounding inactive molecules. Such simplification may be appropriate only for gas-phase reactions and thus is of little relevance to condensed-phase and heterogeneous kinetics. Nevertheless, it is worthy a note that even in the gas-phase reactions the energy barrier height is known [27] to demonstrate a variation with temperature due to temperature dependence of the heat capacity of activation and tunneling effects.

When it comes to condensed-phase kinetics, the processes take place in the liquid or solid medium. In this situation, the energy barrier becomes dependent on the properties of the medium. The size of the barrier may thus change as the properties of the medium change with either temperature or reaction progress. Let us first illustrate [28] a variation with conversion by considering a single-step reaction  $A \rightarrow B$  such as isomerization. In general, the energetic state of the reactant  $A$  is affected by the molecules that surround it. At the early stage of the reaction, when  $\alpha$  is close to 0, the reactant is surrounded by other molecules of  $A$ . As the reaction nears completion (i.e.,  $\alpha$  is close to 1) the reactant will be predominantly surrounded by the product molecules  $B$ . If intermolecular forces between  $A$  and  $A$  are stronger than the forces between  $A$  and  $B$ , the molar enthalpy of  $A$  will be lower in initial ( $\alpha=0$ ) than in final ( $\alpha=1$ ) stages of the reaction (Fig. 1.10). By similar argument, in the final stages ( $\alpha=1$ ) when the product  $B$  is surrounded by the molecules  $B$ , its molar enthalpy is lower than in the initial stages of reaction ( $\alpha=0$ ). Obviously, as this reaction progresses from  $\alpha=0$  to  $\alpha=1$ , its exothermicity should increase and its energy barrier should decrease. In other words, the observed activation energy should progressively decrease as a function of conversion,  $\alpha$ .

A variation of the energy barrier with temperature follows directly from the activated-complex theory developed for reactions of ions or polar molecules in solutions [29]. In accord with this theory, the rate constant of reaction between two ions is given as

$$\ln k = \ln k_0 - \frac{z_A z_B e^2}{\epsilon d_{AB} k_B T}, \quad (1.17)$$

**Fig. 1.10** Illustration of how intermolecular interactions may affect the height of the energy barrier throughout the reaction progress



where  $e$  is the electronic charge,  $z_A$  and  $z_B$  the numbers of charges on the ion,  $\varepsilon$  is the dielectric constant of the medium,  $d_{AB}$  is the distance between the centers of the ions in the activated state, and  $k_B$  is the Boltzmann constant. The energy barrier in Eq. 1.17 includes the dielectric constant, whose temperature dependence causes a variation in the activation energy [29]. In addition, we should note that an elementary step of any chemical reaction is the process of electron transfer. Per the Marcus theory [30, 31], the rate constant of this process is

$$k = A \exp\left(\frac{-\Delta G^*}{k_B T}\right), \quad (1.18)$$

where among several components the free energy of activation,  $\Delta G^*$  involves the solvent reorganization energy, which can vary significantly with temperature [32].

It should be stressed that the aforementioned examples explain variations in the energy barrier for a single-step processes, which is the reaction act itself. The rate of the reaction act is determined by the probability of the reacting molecules to jump over the energy barrier. What is missing from this picture is the rate, at which molecules arrive at the reacting situation or, to put it differently, the rate of molecular mobility or diffusion. If in gases the rate of diffusion is much faster than the rate of the reaction act and thus can be neglected, it is not the case of the condensed media, in which the cohesive forces exert significant resistance to molecular motion.

For example, in liquids the rate of diffusion is inversely proportional to viscosity. The activated-complex theory does not account directly for the effect of viscosity on the reaction rate. However, the effect is treated adequately by the Kramers' theory [33], which introduces viscosity of the medium as a crucial kinetic factor. According to this theory, in the case of large viscosity the rate constant take on the following form:

$$k = k_{ac} \kappa(\eta), \quad (1.19)$$

where  $k_{ac}$  is the activated-complex theory rate constant,  $\kappa(\eta)$  is a term that accounts for the effect of the generalized viscosity on the reaction rate. Extensive testing of the effect demonstrates [34] that  $k$  on  $\eta$  dependencies are strongly nonlinear and, in certain cases, may even be bell-shaped. Considering that viscosity is temperature dependent, the effective activation energy estimated from the temperature dependence of the rate constant (Eq. 1.5) should also be temperature dependent.

Although the activated-complex theory does not account for the diffusion effect of a viscous medium on the reaction rate, the effect can be accounted for by using the so-called addition of kinetic resistances [35]. The idea was originally explored by several workers, including Rabinowitch [36], who proposed that the characteristic time of a process can be defined as the sum of the characteristic time of the reaction act and the characteristic time for reactants to diffuse toward each other. In the simple case of a first-order reaction, the characteristic times can be replaced with the reciprocal rate constants

$$k_{\text{ef}}^{-1} = k^{-1} + k_{\text{D}}^{-1}, \quad (1.20)$$

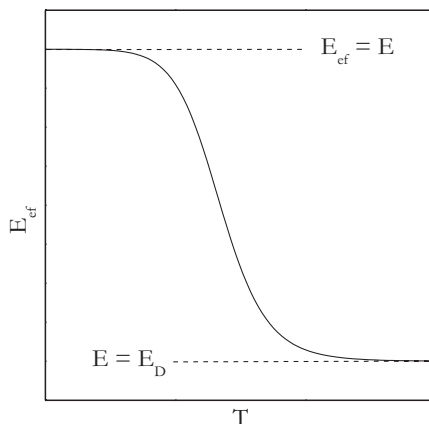
where  $k_{\text{ef}}$ ,  $k$ , and  $k_{\text{D}}$ , respectively, are the effective, reaction, and diffusion rate constants. Assuming that  $k$  and  $k_{\text{D}}$  obey the Arrhenius temperature dependence, we can derive the effective activation energy of the overall process as follows

$$E_{\text{ef}} = -R \left( \frac{d \ln k_{\text{ef}}}{dT^{-1}} \right) = \frac{E_{\text{D}}k + Ek_{\text{D}}}{k + k_{\text{D}}}, \quad (1.21)$$

where  $E$  and  $E_{\text{D}}$  are the activation energies of the reaction and diffusion. In Eq. 1.21,  $E_{\text{D}}$  can be reasonably well approximated by the activation energy of viscous flow [37]. Because both  $k$  and  $k_{\text{D}}$  vary with temperature,  $E_{\text{ef}}$  should generally vary with temperature taking the values between  $E$  and  $E_{\text{D}}$ . Figure 1.11 displays the respective temperature dependence of  $E_{\text{ef}}$  estimated under assumption that  $E_{\text{D}}$  is typically smaller than  $E$ . Equation 1.21 also suggests that  $E_{\text{ef}}$  can be constant in two special cases. First, when diffusion is much faster than the reaction ( $k_{\text{D}} \gg k$ ) the process is said to occur in the reaction regime, and the value of  $E_{\text{ef}} = E$ . Second, when the process occurs in the diffusion regime ( $k \gg k_{\text{D}}$ ) then  $E_{\text{ef}} = E_{\text{D}}$ . The effect of diffusion is equally important for reactions of solids such as decomposition or oxidation when escape of a gaseous product or delivery of gaseous reactant can be controlled by diffusion through a solid product formed on the surface of a solid reagent [38].

All in all, we should recognize that strong intermolecular interactions encountered in condensed-phase media generally affect a single reaction step to such extent that its kinetics depends on the reaction medium properties and the energy barrier varies as these properties change with conversion and/or temperature. Furthermore, a single reaction step can be complicated by additional steps such as diffusion. Then the kinetics of the overall process that involves a reaction and diffusion step becomes driven by two energy barriers. The temperature dependence of such pro-

**Fig. 1.11** Temperature variation of the effective activation energy of a process, whose overall rate is determined by the rate of both diffusion and reaction (Eq. 1.20)





cess gives rise to the effective activation energy, whose value is a temperature- and/or conversion-dependent function of the activation energies of the individual steps. This holds true for any multistep process regardless of whether it involves diffusion or not. For example, if a reaction involves two competing steps, its rate is described by the following equation

$$\frac{d\alpha}{dt} = k_1(T)f_1(\alpha) + k_2(T)f_2(\alpha). \quad (1.22)$$

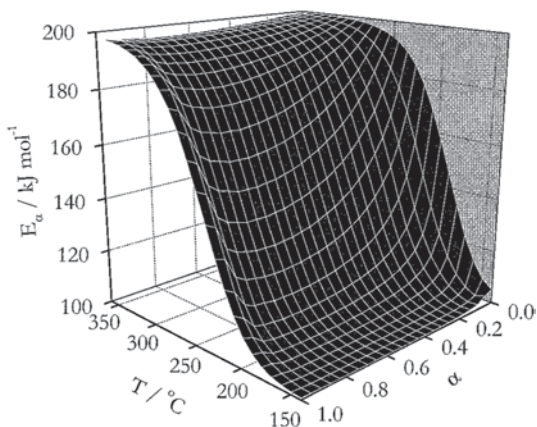
The effective activation energy of such reaction can be determined by taking the logarithmic derivative of the reaction rate at a constant extent of conversion (cf., Eq. 1.13):

$$E_\alpha = -R \left[ \frac{\partial \ln(d\alpha / dt)}{\partial T^{-1}} \right]_\alpha = \frac{E_1 k_1(T) f_1(\alpha) + E_2 k_2(T) f_2(\alpha)}{k_1(T) f_1(\alpha) + k_2(T) f_2(\alpha)}. \quad (1.23)$$

This equation clearly suggests that the effective activation energy depends on both temperature and extent of conversion. An example of the dependence is displayed in Fig. 1.12. The dependence has been simulated [39] by using the activation energies and reaction models experimentally established for the two competing steps in the thermal decomposition of nickel formate. It should also be noted that the occurrence of multiple steps is the most common reason why the activation energy experimentally determined for a condensed-phase reaction happens to be variable.

Although examples of variable activation energy are plentiful, we finish by mentioning the one that has a special significance. It is the inversion of sucrose. As widely accepted [40], the birth of chemical kinetics is marked by the work of Wilhelmly, who in 1850 measured the rate of this reaction. It seems symptomatic that this initial reaction later became known [41] as having variable activation energy.

**Fig. 1.12** Process that involves two parallel reactions having the following kinetic triplets:  $f_1(\alpha) = (1 - \alpha)^{2/3}$ ,  $E_1 = 200 \text{ kJ mol}^{-1}$ ,  $A_1 = 10^{16} \text{ min}^{-1}$  and  $f_2(\alpha) = \alpha(1 - \alpha)$  and  $E_2 = 100 \text{ kJ mol}^{-1}$ ,  $A_2 = 10^7 \text{ min}^{-1}$ . (Reproduced from Vyazovkin [39] with permission of Taylor & Francis)

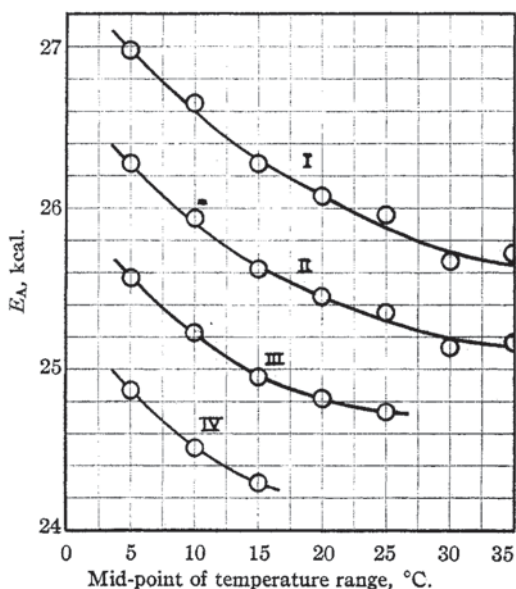


The effect is illustrated in Fig. 1.13. It appears that oftentimes revealing the variability is a matter of time as well as of having the proper tools. Undoubtedly, the isoconversional method is one of such tools.

A frequently asked question is what is a meaning of variable activation energy? Some people believe that the variability of the effective activation energy deprives it of a physical meaning. To be fair, one should first state what the expected physical meaning is. Oftentimes, the expected meaning is the height of a single and constant energy barrier. However, as we showed earlier, this is not a very realistic expectation, and this is the meaning that variable activation energy can only deliver when it is found to be invariable, which is a possible experimental outcome. In our opinion, variable activation energy is physically meaningful as long as it can be explained in terms of the activation energies for individual steps of the overall process (cf., Eq. 1.21 or 1.23).

To reinforce the point, we can draw an analogy with another widely used effective physical property: the atomic masses of elements. From theory we know that an atom contains a certain number of protons and neutrons whose total mass constitutes the mass of an atom. Since to a high degree of accuracy the mass of either proton or neutron is 1 Da, the atomic masses of elements should be practically integer numbers. However, the actual atomic masses that we find in a periodic table rarely agree with this theoretical expectation because they are effective masses averaged over the natural abundances of isotopes encountered on Earth. Although these effective masses cannot be interpreted within a concept of a single atom, they are by no means physically meaningless parameters. Rather, they are the masses that matter practically.

**Fig. 1.13** Effect of temperature on the activation energy of sucrose inversion, not catalyzed (I) and catalyzed by hydrochloric acid of different concentrations (II 1M, III 2M, IV 3M). (Reproduced from Leininger and Kilpatrick [41] with permission of ACS)



### 1.3 Obtaining Computation-Worthy Data

*...and many a good experiment, born of good sense, and destined to succeed, fails, only because it is offensively sudden.*

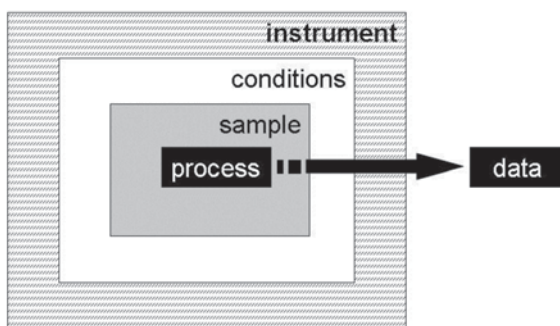
Ralph Waldo Emerson, *The Conduct of Life*

Before investing the time and effort in performing kinetic computations, one should invest both in obtaining computation-worthy experimental data. Neither conditions of kinetic runs should be selected arbitrarily nor should the sample shape and size be chosen randomly. The actual measurements should be preceded by exploratory runs, whose purpose is to reveal the effects of the sample and conditions on the kinetic data as well as repeatability of the measurements. The idea is to arrange the sample and conditions so that small changes in them have little or no effect on the kinetic data. Since it is rarely possible to obtain kinetic data that are entirely independent of the conditions and sample, one has to make sure that throughout the whole series of measurements the conditions and sample are well defined and controlled and that their effects on the kinetics are known. Only in this case one can obtain computation-worthy data, i.e., the data that are adequate to the actual kinetics of a process under study.

Although the aforementioned general approach to obtaining computation-worthy data may seem simple, concrete ways of accomplishing this goal depend on the type of a process studied. For practical advice on how to collect adequate kinetic data for a variety of processes, one is recommended to get acquainted with the recommendations [42] of the ICTAC Kinetics Committee. Here, we discuss briefly some basic rules that must be kept in mind when designing kinetic experiments.

There are two constituents of kinetics measurements that control the adequacy of kinetic data to the process kinetics: sample and instrument. This is obvious from the procedure of data production schematically shown in Fig. 1.14. Because a process is necessarily confined to the sample, the sample parameters unavoidably affect the process conditions. At the same time, the instrument controls a set of conditions the sample is exposed to. The adequacy of kinetic data is accomplished only when both sample and instrument defined conditions are controlled properly. The instrument-defined conditions include the temperature, the rate of temperature change (i.e., the

**Fig. 1.14** The process of data production. The sample, conditions, and instrument unavoidably affect the data and may distort their adequacy to the process. (Reproduced from Vyazovkin et al. [42] with permission of Elsevier)



heating or cooling rate), the gas atmosphere and its flow rate, and the pressure. The sample-defined conditions include the sample form and size as well as a sample holder (pan or crucible).

To understand better the role of all these conditions on the kinetics, we need to start by reviewing the basic kinetic equation. Most commonly it is written and used in the form of Eq. 1.1 that ignores a pressure-dependent term,  $h(P)$ . A more accurate form of the basic kinetic equation is:

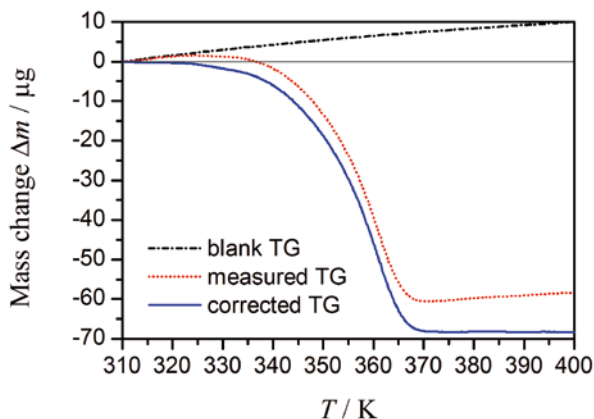
$$\frac{d\alpha}{dt} = k(T)f(\alpha)h(P). \quad (1.24)$$

Experimentally measured rate is adequate to the actual process kinetics only when the process variables ( $\alpha$ ,  $T$ , and  $P$ ) are controlled accurately and precisely. Ignoring  $h(P)$  in Eq. 1.24 is equivalent to assuming that it remains constant during the run. This is a reasonable assumption for a process that does not involve gaseous reactants and/or products, e.g., crystallization. Otherwise, the process may be dependent on the partial pressure of the gaseous reactant and/or product. If a process involves a gaseous reactant as in the case of oxidation of solids or liquids, the constancy of  $h(P)$  is accomplished by securing a large excess of the gaseous reactant supplied at a sufficiently high flow rate. If a process produces a gaseous product that may be reactive toward the reactant or the product as in the case of autocatalytic and reversible reactions, the constancy of  $h(P)$  is accomplished by effectively removing gaseous products with a sufficiently high flow rate of a purge gas. The actual constancy of  $h(P)$  should be tested by conducting a few runs at significantly different flow rates of either reactive or purge gas. If the assumption  $h(P)=\text{const}$  holds, the kinetic curves of  $\alpha$  or  $d\alpha/dt$  versus time should not demonstrate any systematic shifts with increasing the flow rate.

The proper instrumental control of  $\alpha$  means that the signals used to calculate  $\alpha$ , i.e., the heat flow in DSC or the mass in TGA are measured accurately. The accuracy is secured via calibration. The heat calibration of DSC is performed by measuring the heats of melting of reference substances (ice, indium, zinc, aluminum, etc.). The TGA balance is usually capable of self-calibration. However, this calibration is insufficient because it is done at an ambient temperature and, thus, disregards the temperature dependence of the upward buoyant (Archimedes) force, which is proportional to the density of the gas surrounding the sample. When the temperature increases, the gas density decreases diminishing the buoyant force so that the sample mass appears increasingly heavier (Fig. 1.15). The resulting systematic error is eliminated by performing a blank TG run on an empty sample pan and then subtracting the resulting blank TG curve from the TG curve measured by having placed a sample in the same pan (Fig. 1.15).

The proper control of the sample temperature is accomplished by controlling both instrument and sample. The sample temperature is determined by the rate of heat transfer from the instrument-controlled furnace into the sample. Because of the limited thermal diffusivity of the sample, its temperature lags behind that of the

**Fig. 1.15** TGA curves for an empty pan (blank TG) and 555  $\mu\text{g}$  sample of calcium oxalate monohydrate placed in this pan (measured TG). Corrected TG is obtained by subtracting blank TG from measured TG. TGA thermogravimetric analysis. (Reproduced from Vyazovkin et al. [42] with permission of Elsevier)



furnace. The temperature lag is accounted for by temperature calibration. Temperature calibration of DSC is normally done by measuring the melting temperatures of reference substances, e.g., metals. The same approach is used for temperature calibration of TGA instruments capable of measuring the differential thermal analysis (DTA) or DSC signal. Alternatively, one can heat ferromagnetic materials (e.g., alumel, nickel, cobalt, etc.) in a sample pan while placing a magnet under or above the furnace [43]. The temperature of the mass jump that occurs during the ferromagnetic to paramagnetic transition is then identified with the Curie temperature of the material. Another option is to use a dropping weight (platinum coil) connected to the balance beam by a fusible link, which is a thin wire made of melting point metal standard [44].

Temperature calibration is done in a certain temperature range and under certain heat transfer conditions: heating rate, gas atmosphere, pan material, and sample substance. These are the range and conditions for which the calibration holds most accurately. Thus, it should be performed in the temperature range and under the conditions that are as close as possible to those of the actual kinetic runs. In particular, this means that when nonisothermal runs are carried out at several heating rates, the calibration should be conducted in the whole range of the heating rates used. Using the same pans and gas atmosphere for both calibration and measurement are easy conditions to satisfy. It is rarely possible to calibrate the instrument by using substances whose thermal diffusivity is similar to that of the actual sample. Typical calibration standards are metals whose thermal diffusivity is significantly larger than that for most of inorganic and, especially, organic and polymeric samples. This means that the actual sample may still experience some temperature lag unaccounted by calibration.

Another important reason why the sample temperature deviates from the furnace temperature is the sample self-heating/cooling due to the thermal effect of the process. Due to its limited thermal diffusivity, the sample cannot exchange the process heat with the surroundings instantaneously. As a result, a temperature gradient arises within the sample. This temperature deviation cannot be accounted for

via calibration, but it can be reduced by adjusting the sample size and its form. To secure a quick and uniform distribution of heat and, thus, to minimize the temperature deviation of the sample temperature, the sample should form a thin (not thicker than a few 100 microns) uniform layer on the pan bottom. The heat exchange with the surroundings is also accelerated by employing pans made from materials of high thermal diffusivity. Note that the latter decreases about 200 times in the row: Al, Pt,  $\text{Al}_2\text{O}_3$ , steel, quartz, and glass.

To decrease further the temperature gradients due to the thermal effect of the process, one needs to decrease the total amount of heat produced by the process and the rate of its production. The total amount of heat is decreased by keeping the sample mass as small as possible. Considering the sensitivity of modern DSC and TGA instruments, one normally needs no more than a few mg of a sample. The rate of heat production is reduced by keeping the process rate slower. Slower rate is accomplished by using lower temperatures in isothermal runs and slower heating (or cooling) rates in nonisothermal runs. The values of temperatures and heating rates should be selected so that a process of interest is studied in a reasonably wide temperature range, preferably not narrower than 20–40°C. Wide temperature ranges are easy to cover in a series of nonisothermal runs, in which the fastest heating rate is about ten times greater than the slowest. Typically, the heating rates are selected to be within the range 1–20°C min<sup>-1</sup>. The initial and final temperature of the run should be selected, respectively, ~50°C below the temperature at which the process starts and ~50°C above the temperature at which it ends. This would secure accurate determination of the baseline signals.

Covering a wide range of temperatures in isothermal runs presents a certain challenge. The maximum temperature is limited due to the presence of the heat-up period, during which the sample reaches the preset isothermal temperature. The sample unavoidably transforms during this period so that when the temperature sets in, the  $\alpha$  value is already larger than zero. The maximum isothermal temperature should be selected so that the total process time is much longer (e.g., 100 times) than the heat-up time. Once the maximum temperature is identified, other temperatures can be selected by a simple approximate rule: Decreasing the temperature by 10°C decreases the process rate by two to three times. That is, if at the maximum temperature a process takes 1 h to complete, at 20°C lower temperature its completion would take about 4–9 h. Since the process becomes so much slower, the minimum temperature is limited by acceptable length of experiment and detection limit of the instrument.

Whatever the range of the temperatures or heating rates is chosen, one needs to conduct the runs at four to five different temperatures or heating rates. At the very least, one has to conduct runs at three temperature programs. It should however be noted that this would yield the Arrhenius or a similar linear kinetic plot that has only three points on it. From the statistical standpoint, such a plot can be accepted as linear with 95% confidence only when its respective correlation coefficient,  $r$  is greater than 0.997 ( $r^2=0.994$ ), which is frequently not the case. At four and five points, the respective critical values of  $r$  are more reasonable: 0.950 and 0.878. Another argument in favor of more than three runs is that increasing the number of points makes it easier to detect possible nonlinearity of the Arrhenius type of plots.

This is important as one of the ways to reveal the temperature dependence of the activation energy.

Last but not least, when selecting the temperature range for kinetic experiments one should be mindful of possible phase transitions (e.g., melting or solid–solid transformations of the solid reactant) that a reactant may undergo within that range. For example, the respective rates and Arrhenius parameters for solid- and for liquid-state decomposition can differ substantially [45], although they may also remain practically unchanged [46]. Significant changes in the reactivity may also be encountered due to the solid–solid phase transitions. This phenomenon is known as the Hedvall effect [47, 48]. Therefore, one needs to exercise great care when combining kinetic data collected in the temperature ranges below and above the phase transition temperature. To detect the presence of possible phase transitions, one has to carry out a DSC run because they are undetectable by TGA.

The aforementioned techniques allow one to minimize deviations of the sample (process) temperature from the reference (furnace) temperature. Nevertheless, some smaller deviations would continue to be present as long as a process is accompanied by a thermal effect. It is good practice to compare the sample temperature against the reference one. Both values are usually made available by modern DSC and TGA instrumentation. The smaller the difference between the two temperatures the better but it should not exceed 1–2 °C, if the kinetic calculations are to be conducted by means of the isoconversional methods that rely on the reference temperature. When the difference is larger, one should consider reducing the sample mass and/or decreasing the heating rates of nonisothermal runs or the temperatures of isothermal ones. Larger temperature deviations can be tolerated [42, 49] when using the isoconversional methods that permit directly using the sample temperature. A detailed discussion of such methods is provided in Chap. 2.

## References

1. Vyazovkin S, Goryachko V, Bogdanova V, Guslev V (1993) Thermolysis kinetics of polypropylene on rapid heating. *Thermochim Acta* 215:325–328
2. Bonnet E, White RL (1998) Species-specific isoconversion effective activation energies derived by thermogravimetry-mass spectrometry. *Thermochim Acta* 311:81–86
3. Ramis X, Salla JM, Mas C, Mantecón A, Serra A (2004) Kinetic study by FTIR, TMA, and DSC of the curing of a mixture of DGEBA resin and  $\gamma$ -butyrolactone catalyzed by ytterbium triflate. *J Appl Polym Sci* 92:381–393
4. White DR, White RL (2008) Isoconversion effective activation energy profiles by variable temperature diffuse reflection infrared spectroscopy. *Appl Spectr* 62:116–120
5. Badrinarayanan P, Zheng W, Simon SL (2008) Isoconversion analysis of the glass transition. *Thermochim Acta* 468:87–93
6. Madbouly SA, Otaigbe JU (2006) Kinetic analysis of fractal gel formation in waterborne polyurethane dispersions undergoing high deformation flows. *Macromolecules* 39:4144–4151
7. Ramis X, Cadenato A, Morancho JM, Salla JM (2003) Curing of a thermosetting powder coating by means of DMTA, TMA and DSC. *Polymer* 44:2067–2079
8. van den Beukel A (1986) Analysis of chemical short range ordering in amorphous  $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$ . *J Non-Cryst Solids* 83:134–140

9. Brown ME (2001) Introduction to thermal analysis, 2nd edn. Kluwer, Dordrecht
10. Wunderlich B (2005) Thermal analysis of polymeric materials. Springer, Berlin
11. Menczel JD, Prime RB (eds) (2009) Thermal analysis of polymers: fundamentals and applications. Wiley, Hoboken
12. Atkins P, de Paula J (2010) Physical chemistry, 9th edn. W.H. Freeman, New York
13. Khawam A, Flanagan DR (2006) Solid-state kinetic models: basics and mathematical fundamentals. *J Phys Chem B* 110:17315–17328
14. Vyazovkin S, Wight CA (1999) Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data. *Thermochim Acta* 340/341:53–68
15. Vyazovkin S, Linert W (1995) False isokinetic relationships found in the nonisothermal decomposition of solids. *Chem Phys* 193:109–118
16. Criado JM, Ortega A, Gotor F (1990) Correlation between the shape of controlled-rate thermal analysis curves and the kinetics of solid-state reactions. *Thermochim Acta* 157:171–179
17. Criado JM, Perez-Maqueda LA (2005) Sample controlled thermal analysis and kinetics. *J Therm Anal Calorim* 80:27–33
18. Brown ME, Maciejewski M, Vyazovkin S, Nomen R, Sempere J, Burnham A, Opfermann J, Strey R, Anderson HL, Kemmler A, Keuleers R, Janssens J, Desseyn HO, Li CR, Tang TB, Roduit B, Malek J, Mitsuhashi T (2000) Computational aspects of kinetic analysis. Part A: the ICTAC kinetics project—data, methods and results. *Thermochim Acta* 355:125–143
19. Maciejewski M (2000) Computational aspects of kinetic analysis. Part B: the ICTAC kinetics project—the decomposition kinetics of calcium carbonate revisited, or some tips on survival in the kinetic minefield. *Thermochim Acta* 355:145–154
20. Vyazovkin S (2000) Computational aspects of kinetic analysis. Part C: the ICTAC kinetics project—the light at the end of the tunnel? *Thermochim Acta* 355:155–163
21. Burnham AK (2000) Computational aspects of kinetic analysis. Part D: the ICTAC kinetics project—multi-thermal—history model-fitting methods and their relation to isoconversional methods. *Thermochim Acta* 355:165–170
22. Vyazovkin S, Burnham A K, Criado JM, Pérez-Maqueda LA, Popescu C, Sbirrazzuoli N (2011) ICTAC kinetics committee recommendations for performing kinetic computations on thermal analysis data. *Thermochim Acta* 520:1–19
23. Vyazovkin SV, Sbirrazzuoli N (2006) Isoconversional kinetic analysis of thermally stimulated processes in polymers. *Macromol Rapid Commun* 27:1515–1532
24. Friedman HL (1964) Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. *J Polym Sci Part C* 6:183–195
25. Vyazovkin S, Wight CA (1998) Isothermal and non-isothermal kinetics of thermally stimulated reactions of solids. *Int Rev Phys Chem* 17:407–433
26. Eyring H (1935) The activated complex and the absolute rate of chemical reactions. *Chem Rev* 17:65–77
27. Hulett JR (1964) Deviations from the Arrhenius equation. *Quart Rev* 18:227–242
28. Vyazovkin S, Wight CA (1997) Kinetics in solids. *Annu Rev Phys Chem* 48:125–149
29. Glasstone S, Laidler KJ, Eyring H (1941) The theory of rate processes. McGraw-Hill, New York
30. Marcus RA (1964) Chemical and electrochemical electron transfer theory. *Annu Rev Phys Chem* 15:155–196
31. Marcus R A (1993) Electron transfer reactions in chemistry. Theory and experiment. *Rev Mod Phys* 65:599–610
32. Vath P, Zimmt MB, Matyushov DV, Voth GA (1999) A failure of continuum theory: temperature dependence of the solvent reorganization energy in highly polar solvents. *J Phys Chem B* 103:9130–9140
33. Kramers HA (1940) Brownian motion in a field of force and the diffusion model of chemical reactions. *Physica* 7:284–304
34. Schroeder J, Troe J (1993) Solvent effects in the dynamics of dissociation, recombination, and isomerization reactions. In: Fleming GR, Hänggi P (eds) Activated barrier crossing. World Scientific, Singapore, pp 206–240



35. Frank-Kamenetskii DA (1969) Diffusion and heat transfer in chemical kinetics, 2nd edn. Plenum Press, New York
36. Rabinowitch E (1937) Collision, co-ordination, diffusion and reaction velocity in condensed systems. *Trans Faraday Soc* 33:1225–1233
37. Vyazovkin S, Sbirrazzuoli N (2000) Effect of viscosity on the kinetics of initial cure stages. *Macromol Chem Phys* 201:199–203
38. Vyazovkin SV (1993) An approach to the solution of the inverse kinetic problems in the case of complex reactions. IV. Chemical reaction complicated by diffusion. *Thermochim Acta* 223:201–206
39. Vyazovkin S (2000) Kinetic concepts of thermally stimulated reactions in solids: a view from a historical perspective. *Int Rev Phys Chem* 19:45–60
40. Laidler KJ (1987) *Chemical kinetics*, 3rd edn. Harper Collins, New York
41. Leininger PM, Kilpatrick M (1938) The inversion of sucrose. *J Am Chem Soc* 60:2891–2899
42. Vyazovkin S, Chrissafis K, Di Lorenzo ML, Koga N, Pijolat M, Roduit B, Sbirrazzuoli N, Suñol JJ (2014) ICTAC kinetics committee recommendations for collecting experimental thermal analysis data for kinetic computations. *Thermochim Acta* 590:1–23
43. Gallagher PK, Blaine R, Charsley EL, Koga N, Ozao R, Sato H, Sauerbrunn S, Schultze D, Yoshida H (2003) Magnetic temperature standards for TG. *J Therm Anal Calorim* 72:1109–1116
44. McGhie AR, Chiu J, Fair PG, Blaine RL (1983) Thermogravimetric apparatus temperature calibration using melting point standards. *Thermochim Acta* 67:241–250
45. Bawn CEH (1955) Decomposition of organic solids. In: Garner WE (ed) *Chemistry of the solid state*. Butterworth, London, pp 254–267
46. Vyazovkin S, Clawson JS, Wight CA (2001) Thermal dissociation kinetics of solid and liquid ammonium nitrate. *Chem Mater* 13:960–966
47. Hedvall JA (1934) Changes in crystal structure and their influence on the reactivity and catalytic effect of solids. *Chem Rev* 15:139–168
48. Gallagher PK, Sanders JP (2003) Ceramics, glass, and electronic materials. In: Brown ME, Gallagher PK (eds) *The handbook of thermal analysis & calorimetry, vol 2. Applications to inorganic and miscellaneous materials*. Elsevier, Amsterdam, pp 191–260
49. Vyazovkin S (1997) Evaluation of the activation energy of thermally stimulated solid-state reactions under an arbitrary variation of the temperature. *J Comput Chem* 18:393–402