

# An introduction

# to n-th order and autocatalysis reactions

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# 1. Introduction to thermokinetics

Chemical kinetics is an important branch of modern physical chemistry. It extracts rules from various actual chemical reactions, studies the reactions from a reaction rate and reaction mechanism view, and concludes into a series of important parameters like time, temperature, concentration, pressure, catalyst, solution, etc.

Thermokinetics is a simplification of chemical kinetics. It correlates strongly with thermal analysis techniques like DSC & TGA, simplifies or combines parameters which cannot be easily studied with thermal analysis methods, and finally characterizes the reaction rate simply as a function of time, temperature & conversion. The basic thermokinetics equation in derivative form is:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \tag{1}$$

This function is used to describe the following formal reaction:

$$A \xrightarrow{t,T,\alpha} B \qquad (2)$$

Here, t is time, T is temperature, and  $\alpha$  is the normalized conversion percentage.  $d\alpha/dt$  is the rate of conversion change with time; in the scope of classical thermokinetics, it only depends on the following two functions:



 $\mathbf{k}(\mathbf{T})$ : rate constant, the dependency of the reaction rate on temperature. Normally it takes the form of the Arrhenius equation:

$$k(T) = A \cdot e^{-E_a/RT} \qquad (3)$$

Here Ea is formal activation energy in kJ/mol. From a physical chemistry perspective, this parameter corresponds with the reaction's energy barrier. It also corresponds with the change of reaction rate as a function of temperature. A is a direct proportion factor, which is called the pre-exponential factor or frequency factor. R is the gas constant, which has the value of 8.314 J/(mol\*K).

 $f(\alpha)$ : reaction type, also called mechanism function or reaction type. It represents the dependency of the reaction rate on conversion, and can be treated as a mathematical description of the reaction mechanism. This part is the most versatile; there are a lot of functions to mathematically describe different reaction mechanisms. The functions most commonly used can be classified into five categories: n-th order reaction, autocatalysis reaction, phase-boundary reaction, nucleation-growth reaction and diffusion barrier reaction. Each category includes a few different functions to refine the description for different reaction mechanisms.

As for other parameters from chemical kinetics, either they are omitted<sup>1</sup>, or normalized<sup>2</sup>, or combined into proportion factor  $A^3$ , exponential factor  $Ea^4$  and mechanism function<sup>5</sup>.

- 1. e.g., most thermal analysis measurements are under normal pressure, so P is omitted here.
- 2. e.g., the relative change in concentration is normalized to "conversion" between 0...1.
- 3. the factors which influence the molecular-contact frequencies like mole concentration, viscosity of reaction system, cross-section-area of molecule, etc.
- 4. so Ea is called "apparent activation energy" and could differ from the true activation energy in the chemical sense.
- 5. e.g., the geometry property of the reaction interface.

So, thermokinetics is essentially a kind of phenomenological science which is used to mathematically abstract and treat data from various thermal analysis measurement results. Take the TGA curve as an example: Since the mass loss percentage (100%  $\rightarrow$  x%) can be easily converted to conversion  $\alpha$  (0  $\rightarrow$  1), a TGA curve is essentially a certain ( $\alpha$ , t, T) function, and by derivative calculation one can obtain the conversion rate  $d\alpha/dt$  (like DTG in shape). Similarly to this, after certain corrections, the partial peak area of the DSC signal can be converted to conversion, and after derivative calculation one will obtain the conversion rate (like DSC in shape): see Fig.1.





Fig.1 Measured heat flow dQ/dt, degree of conversion  $\alpha(t)$ , and the formal reaction rate  $d\alpha/dt$ .

So, no matter whether the curves are TGA or DSC, they can all be treated as  $(d\alpha/dt, \alpha, t, T)$  relation curves and can be put into equation(1) to solve out the kinetics parameters. Classified by different solving methods, the approaches are model-free analysis and model-based analysis. No matter which method is used, the objective is always to obtain the kinetics parameters including Ea, A & a certain  $f(\alpha)$ ; i.e., to find out a complete thermokinetics function which only contains three variables  $(t, T, \alpha)$ . This set of parameters is called *Kinetics Triplet*. Then the reaction progress ( $\alpha \& d\alpha/dt$ ) with the evolvement of time (t), temperature (T) & heating rate ( $\beta = dT/dt$ ) can be regarded as known. Starting from this thermokinetics function, we can predict the reaction behavior under different process temperature programs, or we can optimize the process temperature program following certain rate-control demands so as to provide guidance for actual process programs and obtain the expected reaction progress.

Above is a brief yet panoramic introduction for themokinetics. As a branching science starting from physical chemistry while combining real-world measurement techniques, there are many issues that can be discussed; in the short article, we would only like to discuss two kinds of mechanism functions: n-th order & autocatalysis reaction, which you may often encounter in homogeneous reaction systems.

#### 2. Homogeneous reaction system

A homogeneous reaction system is a kind of ideal reaction system where the reactant molecules evenly distribute in the system; in a macroscopic sense, there are no significant concentration differences in different regions, and for every time point, the reaction rate is the same throughout the system. In this kind of reaction system, besides temperature, the only dominant factor for reaction rate is the molecular concentration along with the change therein.

In contrast, a heterogeneous (sometimes also called inhomogeneous) reaction system has a clear concept



of the reaction interface, and the molecular reactions only occur on interfaces of this kind. In this kind of system, the change in concentration is no longer the dominant factor for reaction rate; in fact, outside of the interface, the reactant always maintains the initial concentration and the reaction rate is always zero. Besides temperature, the factor which dominates the reaction rate with respect to the interface is simply the geometry property of the interface itself, together with its evolution over time (expanding, contracting, thickening) and space (one-dimensional, two-dimensional, three-dimensional).

Both homogeneous and heterogeneous systems are ideal mathematical models. The real chemical reaction systems are often more complicated, but for small-sized reactions (like thermal analysis measurements with ~10mg sample amount), and under the assumption of idealized mass & heat transfer, most reactions can be attributed to one of these two systems. In the field of thermal analysis, normally the uniform liquid-phase reactions (like reactions in solution) can be classified as homogeneous reactions, whereas the reactions involving multi-phases (gas/solid, liquid/solid, gas/liquid, solid/solid, liquid/liquid) shall be heterogeneous, but some uniform solid-phase reactions with no clear concept of reaction interface sometimes can also be simplified to a homogeneous model. Once the kinetic model for a small-sized reaction system is obtained, a further correction for mass and heat transfer must be applied in order to scale up for actual industry application.

Note: Here, the terms 'homogeneous' and 'heterogeneous' only refer to the phase states of reactant and product; it is irrelevant whether the material composition is chemically pure substance or not. One example would be the crystallization of a solid: Although the material may be "pure" in the chemical sense, if the phase state of the crystallized region differs from that of the amorphous region, the reaction is heterogeneous. Another example is the curing of fiber-reinforced resin. Although macroscopically the material is a composite containing various compositions (resin, fiber, etc.), on a smaller scale the distribution of fiber may also not be so uniform, however, if one ignores the interaction of resin and fiber, and supposes the curing reaction only takes place within the liquid resin, then it can still be classified as a homogeneous reaction.

#### 3. n-th order reaction

The n-th order reaction is the simplest and also most commonly used homogeneous reaction model. Here, the consumption of reactant molecules is taken as the only influencing factor for reaction rate. The common function is:

$$f(\alpha) = (1 - \alpha)^n \tag{4}$$

Here, the relative change in reactant concentration is normalized to conversion  $\alpha$ :

$$\alpha = \frac{c_0 - c}{c_0 - c_1} \tag{5}$$

where  $c_0$  is the initial concentration,  $c_1$  is the final concentration and c is the current concentration of reactant.

For example, the reactant's initial concentration is 0.7 mol/L; after the reaction finishes, this is reduced to 0.2 mol/L (in the real world, the reactant is often not 100% consumed after the reaction). Then the relative change in concentration will be normalized to "conversion" between 0...1, i.e. in Table1:



Mole concentration mol/L	Conversion $\alpha$ (dimensionless)	1 - α
0.7	0	1
0.6	0.2	0.8
0.5	0.4	0.6
0.4	0.6	0.4
0.3	0.8	0.2
0.2	1.0	0

Table1. Recalculation from mol/L concentration to conversion a and relative amount of reactant (1-a)

Here  $1-\alpha$  corresponds to the relative amount of reactant at any given point in time during the reaction, but it seems that the information about absolute mole concentration has been lost. However if the reactant concentration is 7mol/L instead of 0.7 mol/L then the higher concentration has a strong impact on the reaction rate, but this influence has been detached and ascribed into the proportional factor A. For the reaction system with a higher mole concentration, the probability of molecule-contact will be higher within a certain time period; that is to say, the frequency of chemical reaction is higher, so the frequency factor A will also be larger. So, if one uses the classical thermokinetics method to build a model for the same reaction with a different mole concentration, the frequency factor may differ; the researcher should pay attention to this.

For a homogeneous reaction system, there are two commonly used n-th order reactions with integer reaction order and clear physical/chemical sense:

First order reaction (F1): n = 1,  $f(\alpha) = 1 - \alpha$ ; i.e., if the temperature is fixed, the reaction rate will be directly proportional to the relative remaining amount of reactant, or in other words, as the reactant is consumed, the reaction decelerates at the same ratio. This can often be seen for the monomolecular reaction  $A \rightarrow B$  inside of a homogeneous system, e.g., molecular structural rearrangement, spontaneous decay of radioactive atoms, some liquidus decomposition reactions, etc.

Second order reaction (F2): n=2,  $f(\alpha) = (1 - \alpha)^2$ . If the temperature is fixed, the reaction rate will be proportional to the square of the relative remaining amount of reactant; this is often seen for the dual-molecular reaction in solvents, e.g.,  $2A \rightarrow B$ .

Now let's talk about some mathematics. For the general equation of n-th order reaction (Fn)

$$f(\alpha) = (1 - \alpha)^n \qquad (6)$$

let's discuss the change in f(  $\alpha$  ) versus  $\alpha$  with different reaction orders.



In Figure 2 we can see:

1. For all curves, the maximum value always appears at the starting point. This means for n-th order reactions that if the temperature is fixed, the reaction rate is highest at the beginning, then decreases as the reaction progresses.

2. If n=1 is taken then  $f(\alpha)$  is a diagonal line. If n increases then  $f(\alpha)$  will decrease faster with  $\alpha$ . This indicates with the transition of reactant that if the reaction has a higher reaction order, then the reaction rate will decrease faster. In this Figure the small values of n correspond to phase-boundary reactions of contracting geometry in heterogenius materials.



Fig.2 Dependence of reacton type function  $f(\alpha)$  vs  $\alpha$  for n-th order reaction Fn with different values of n

From a physical chemistry view, the reaction order is always an integer and seldom exceeds 3 (a synthetic reaction participating with more than 3 molecules simultaneously is very rare). But from a formal kinetics view, by mathematical fitting, the reaction order can be non-integer; the value can be higher than 3, or smaller than 1, but this often indicates that the inner reaction mechanism is inhomogeneous or not really chemical. For example, if you use an n-th order function to do a curve fit and the reaction order is higher than 3, this means that the reaction will rapidly decelerate with the transition of the reactant; it could be either a diffusion barrier reaction in which the product accumulates on the interface or not pure chemical reaction. If the reaction order is less than 1, it may be a phase boundary contraction reaction. In such cases, n=2/3 might be a three-dimensional phase boundary reaction with a column-shaped contracting interface; and n=0 (zero order reaction) might correspond to a one-dimensional phase boundary reaction in which the interface area never changes.

#### 4. Auto-catalysis reaction

An auto-catalysis reaction, which belongs to self-accelerating reactions, is a kind of reaction where the reaction rate will increase with the generation of product. The general equation for this is the extended Prout-Tompkins equation (Bna):

$$f(\alpha) = (1 - \alpha)^n \cdot \alpha^m \tag{7}$$

Here  $1-\alpha$  corresponds to the relative amount of reactant,  $\alpha$  corresponds to the relative amount of product, and the reaction rate is the function of the two; the latter will decrease with the consumption of reactant and increase with the generation of product. Some examples in chemistry are curing and cross-linking reactions, fermentation reactions, polymerization reactions, chain reactions, etc.



The simplest auto-catalysis model is the Prout-Tompkins equation (B1):

$$f(\alpha) = (1 - \alpha) \cdot \alpha$$

It is a simplification of Bna (n=1, m=1), and can be used to describe the following reaction:

#### $A + B \rightarrow 2B$

Fig.3 presents the concentration of reactant A and product B for isothermal autocatalytical reaction. Here the reaction rate still decreases with the consumption of A, but once B is generated, it plays another role as reactant which will boost the progress of the reaction. Both curves are sigmoidal, and the sigmoidal shape for degree of conversion for isothermal measurement is the evidence of the reaction with self-acceleration. In the beginning reaction, stage of the when the concentration of B is very low, the reaction rate is low; in the final stage when the concentration of A is already very low, the reaction rate is also low. The maximum of the reaction rate will appear at the stage when the concentrations of both A & B are sufficient, i.e., in the middle stage of the reaction. This rule can be verified by the plotting of equation B1, which is shown in Fig.4.







*Fig 4. Dependence f(α) vs α for simplified Prout-Tompkins autocatalytical reaction B1* 

## 5. How to distinguish between n-th order and auto-catalysis reactions

#### from thermal analysis curves

The distinction between n-th order and auto-catalysis reactions can be seen clearly with isothermal measurements. With fixed temperature, k(T) will be constant, so the kinetics equation can be simplified to:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \tag{8}$$

i.e., the reaction rate  $d\alpha/dt$  will be directly proportional to  $f(\alpha)$ . From the previous discussion we know, that for an n-th order reaction  $f(\alpha)$  decreases with  $\alpha$  monotonously; for an auto-catalysis reaction, the maxima of  $f(\alpha)$  will appear in the middle stage of the reaction. For isothermal measurement we get the change in  $d\alpha/dt$  (for DSC, DTG) over time t; here we must first integrate the equation to obtain  $\alpha(t)$ , then derive to obtain  $d\alpha/dt$  over t.

From a chemical perspective, under isothermal conditions, for an n-th order reaction the reaction rate is



proportional to the concentration of reactant; thus, in the beginning, the concentration of reactant is at its highest and the reaction rate is also at its highest; then, with the consumption of reactant over time, the reaction rate will gradually slow down. As for auto-catalysis reactions, at the beginning the amount of B is quite low and the catalysis effect is not so evident, so at that time the reaction rate is quite slow. With the slow reaction rate, the accumulation of product B is also slow, which causes a long "induction period" with a slow rate at the beginning of the reaction. When the amount of B accumulates to a certain level, the boost effect for the reaction will become evident: As the reaction speeds up, a lot of product B are produced, which further accelerates the reaction; therefore, in the middle stage, the reaction speeds up very fast. In the final stage, with the dramatic consumption of reactant A, the reaction rate will slow down again, until the reaction finishes.

A typical DSC comparison of the two reaction types under isothermal conditions is shown in the Figure 5:



Fig.5 Comparison of isothermal DSC measurements for n-th order reaction (blue) and autocatalytical reaction (green)

This comparison result can be confirmed mathematically by deducing from equation Eq.8 to  $d\alpha/dt$  over t and drawing the plot.

For a dynamic heating test, the complete kinetics equation will be:

$$\frac{d\alpha}{dt} = Ae^{-E_a/RT} \cdot f(\alpha) \tag{9}$$

During heating, besides  $f(\alpha)$ , the influence from the continuous temperature change also exists, and the reaction will also speed up. So even for an n-th order reaction, the maxima rate no longer appears at the starting point.

# 6. Combined auto-catalysis reaction

The single auto-catalysis functions are not so frequently used in real applications. The reason becomes clear if you substitute the Prout-Tompkins reaction type into the thermokinetics equation:

$$d\alpha/dt = k(T) \cdot (1 - \alpha) \cdot \alpha$$
 (10)



At the start of the reaction,  $\alpha = 0$ , so  $d\alpha/dt = 0$ . But if the conversion rate is zero, this means the reaction will not occur;  $\alpha$  will always stay zero!

We'll arrive at the same conclusion if we take the chemical model of the Prout-Tompkins reaction type:

$$A + B \rightarrow 2B \tag{11}$$

To start the reaction, the participation of product B is required. Thus, before the reaction, one must mix a small amount of B into the system; otherwise, if starting from 100% A without B's participation, a first B product will never be generated, which means that the reaction will never occur.

Actually, in a real reaction system, what often occurs is the parallel existence of two reactive paths:

$$\begin{cases} A \to B & (n-th \ order \ path) \\ A+B \to 2B & (auto-catalysis \ path) \end{cases} (12)$$

i.e., A can convert to B by the first pathway, just before the time where the second autocatalytical pathway, under the "catalysis" of B , becomes to be significant.

This kind of reaction can be called a combined Kama-Sourour auto-catalysis reaction. Under the assumption that the activation energies of the two paths are the same, we got the partial case of Eq12, the function Cnm:

$$f(\alpha) = (1 - \alpha)^n \cdot (1 + K_{cat} \cdot \alpha^m) \tag{13}$$

If we look further into the function, we'll see that the reaction rate is presented as the sum of two items, namely Fn and Bna; additionally, there's a weight factor (auto-catalysis factor)  $K_{cat}$  to represent the contribution of Bna, or it can also be said that the frequency factors of the two paths are different.

Simplified versions of Cnm include C1 (both exponents n and m = 1, i.e., the combination of F1 and B1) and Cn (m=0, namely the reaction order of A is n while B plays the role as first-order). Cn is more commonly used.

If assuming the activation energies of the two paths are different, the general Kamal-Sourour reaction type is used:

$$\frac{d\alpha}{dt} = Ae^{-\frac{E_{a1}}{RT}} \cdot (1-\alpha)^n + K_{cat} \cdot Ae^{-\frac{E_{a2}}{RT}} \cdot (1-\alpha)^n \cdot \alpha^m \qquad (14)$$

This reactaion type is the sum of reactions Fn and Bna with a different values of Ea and a certain weight factor (or different frequency factor).

Reactions C1, Cn, Cmn are the simplified case of the general Kamal-Sourour reaction with two competitive pathways. Being the combination of an n-th order and an auto-catalysis reaction, a combined auto-catalysis reaction will exhibit accelerating performance in between that of a pure n-th order reaction and a pure auto-catalysis reaction; i.e., there will be a certain induction period, and after that, the reaction's acceleration will be more significant than n-th order, but not as dramatic as the pure auto-catalysis Prout-Tompkins reaction. Of course, the actual accelerating behavior depends on the combination weight of the two paths.



# 7. Example: Thermocuring of epoxy resin- a comparison of different

#### reaction types

For a homogeneous system, we've already discussed in detail the characteristic reaction progress for different reaction types (n-th order, auto-catalysis, and combined auto-catalysis). Here we will use a DSC example of the curing of epoxy resin; by comparing the kinetics model-fit results, we are trying to help our customers understand the difference between these reaction types visually and intuitively.

Here we carried out DSC tests on curing process of epoxy resin at different heating rates (5, 10, 20 K/min), and obtained the following exothermal curing peaks. The experimental curves are present in the Figure 6:



Fig.6 Three experimental DSC curves for different heating rates

There are some existing articles which prove that the curing of EP is some kind of auto-catalysis reaction [3]. However, here we will put all of these existing conclusions aside and suppose we don't know what's going on chemically inside of the material at all. We'll therefore try to apply different reaction types to carry out curve-fitting, and decide what the possible reaction type is from the fit quality alone.



Fig.7 Kinetics fit of curing curves using reaction of n-th order Fn

In the Fig.7, the points are measured data points, and the lines are calculated fit-optimized curves using n-th order reacton type (Fn). We already know that the DSC signal is directly proportional to the reaction rate.



If we compare the fit curve with the measured curve and focus on the early stage, we find that the n-th order reaction has no obvious induction period and the increase in the reaction rate is relatively smooth, while for the measured signal, the starting part is more horizontal and the later acceleration is more strong (the left side of the peak is sharper than for the fit curve); this indicates that the reaction can involve an auto-catalysis mechanism.



Fig.8 Kinetics fit of curing curves usingautocatalytical Prout-Tompkins reaction Bna

In Fig.8, we'll attempt to use the pure auto-catalysis Prout-Tompkins reaction type, namely Bna, to carry out a curve fit. The overall fit quality is greatly improved, but the early stage of reaction is still not so properly fitted. If we focus on the solid line (fit curve), we'll find that the pure auto-catalysis function has a longer induction period during which the reaction rate is close to zero (nearly a horizontal line); after that, the reaction rate accelerates faster than it does in reality.



Fig.9 Kinetics fit of curing curves using autocatalytic reaction Cn which is the partial case of Kamal-Sourour reacton

Finally, we will use the combined auto-catalysis reaction Cn to carry out a curve fit. In Fig.9, the calculated curve fits almost perfectly with the measured curve; this indicates that the reaction mechanism might possibly be a combination of n-th order and auto-catalysis paths:

$$\begin{cases} A \to B & (Fn) \\ A + B \to 2B & (Bna) \end{cases}$$
(15)



With weighting factor Kcat=1.34. Other parameters listed here: Ea = 46.2 kJ/mollgA = 2.5 lg(1/s)n = 1.7

All these values are in a chemically sensible range, which proves this reaction type is reasonable.

# 8. Conclusion

Thermokinetics is a branch of science which combines chemical kinetics with thermal analysis techniques; it filters and abstracts from the various factors influencing reaction rate, simplifying to a relatively basic function of temperature and conversion. It can be used to mathematically conclude the measurement data, to predict the measurement result under different temperature programs, or to help optimize the process temperature program under a certain rate-control requirement.

The reaction systems can be classified into homogeneous and heterogeneous systems. The common reaction types for homogeneous systems are n-th order and auto-catalysis types. Besides the temperature factor, the rate change in n-th order reactions only follows the consumption of reactants, while the auto-catalysis reaction further introduces the accelerating effect from product generation. In some reaction systems, n-th order and auto-catalysis paths may take place in parallel.

Different reaction types can be described by different reaction models in thermokinetics, and exhibit different behaviors (induction, accelerating, decelerating, etc.) in thermal analysis curves. In circumstances where knowledge regarding chemical mechanisms is lacking, we can try different mechanism functions to carry out curve fitting and compare the results with measured thermal analysis curves. The possible reaction mechanism could thus be surmised based on the fit quality and on whether the obtained kinetics parameters are within a reasonable range.

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