Interrelations of activation energies in thermoanalytical kinetics

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▼ Introduction

Processes in condensed state are extensively studied by thermoanalytical techniques such as TG, DSC, DTA, STA/EGA, chemiluminescence, etc. The mechanisms are very often unknown or too complicated to be characterised by a simple kinetic model and they tend to occur in multiple steps with different rates. The kinetics are described using methods based on the single-step approximation.

Ever since late 1950s there is an apparently endless stream of "novel", "advanced", or "improved" methods for obtaining kinetic parameters from non-isothermal measurements based on the general rate equation

The differences in the values of kinetic parameters calculated using various methods of the same class (integral or incremental) are often below their uncertainties.

Theory — accurate description of the kinetics of a complex process: each elementary reaction step should be described by its own kinetic equation + equations for diffusion and heat transfer — a set of many differential kinetic equations. Obtaining the kinetic parameters = concentrations of all intermediates and products should be measured.

Reality — mechanisms are very often unknown or very complicated for exact description. Usually, only α vs. $T(t)$ is measured.

Way out — most frequent description of thermoanalytical kinetics is based on *single-step approximation*:

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

Meaning — Representation of the kinetics of a complex process via substitution of a generally complex set of kinetic equations by the sole single-step kinetic equation.

Theory of analysis of complex systems — effects of temperature and conversion on the rate of the process are independent of each other.

Our interpretation — Representation of the kinetics of a complex process by substituting a complex set of kinetic equations by the single-step kinetic equation. Therefore:

- $k(T)$ — is **not the rate constant** of the process
- $f(\alpha)$ — **may not reflect the mechanism** of the process
- $k(T)$ and $f(\alpha)$ — just **components of the kinetic hypersurface.** Their parameters in have **no physical meaning in general**.
- Parameters enable us to **recover reaction rate**, T_α and t_α — modeling the kinetics of the process without knowing its detailed mechanism.
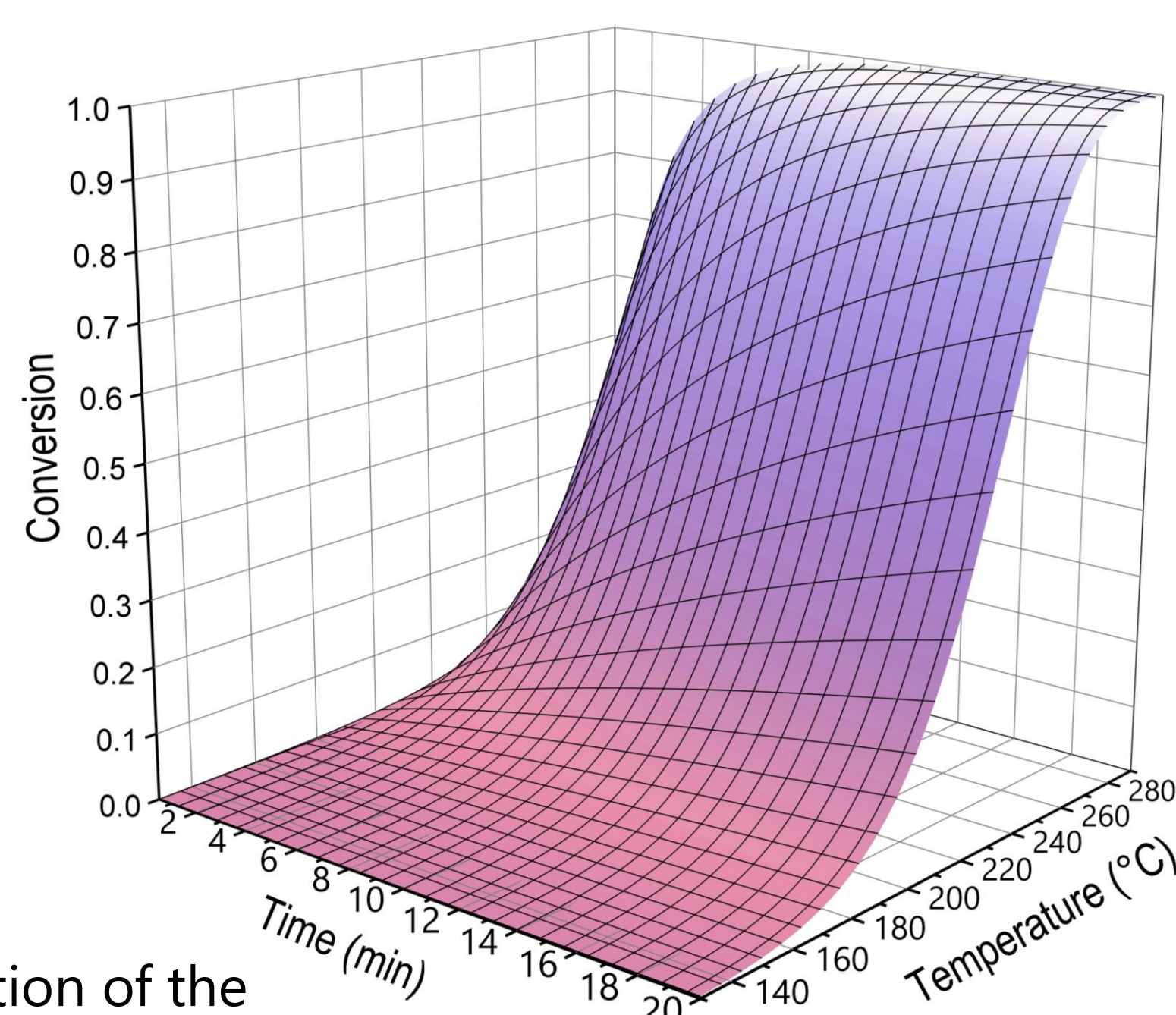

Figure 1. Graphical representation of the kinetic hypersurface in $T{-}t{-}\alpha$ coordinates

▼ Interrelations of activation energies

Among the methods based on Eq. (1), the isoconversional (model-free) ones are most popular, mainly for evaluating experimental results from measurements obtained under several linear heating rates.

In papers published, we often encounter a strange practice of evaluating experiments by several linear methods and comparing the results. Flynn–Wall–Ozawa [2,3] (FWO), Kissinger–Akahira–Sunose [4] (KAS) and Starink [5] methods belong to this group. All these methods are based on the treatment of kinetic results by the relationship

$$\ln\left(\frac{\beta}{T^a}\right) = -b\frac{E}{RT} + c \quad \text{or} \quad \ln\beta = -b\frac{E}{RT} + a\ln T + c \tag{2}$$

where β is the heating rate, T is the isoconversional temperature, E is the apparent activation energy and a, b, c are constants depending on the approximation applied for the calculation of temperature integral [1]. If we consider the a and b values for individual methods, we can be obtain by differentiating of $d(\ln\beta)/dT$:

$$1.058E_{\text{FWO}} = E_{\text{KAS}} + 2RT = 1.0037E_{\text{Starink}} + 1.8RT \tag{3}$$

From Eq. (3) we can see that the activation energies from FWO, KAS and Starink methods are interrelated, and it makes no sense to make far-reaching conclusions from their comparison.

The authors also frequently overlook that the differences between the methods are below the uncertainty of E. Apart from "deterministic" differences in the E values given by Eq. (3), different transformations applied to experimental data in these methods lead to additional random scatter in the resulting E values, thus making their comparison even more meaningless. Moreover, all the three methods are integral and they are mathematically incorrect in the case of variable activation energy [6].

▼ Another „bad kinetic habit"

The activation energies are often seen as the ultimate goal of any kinetic study and conclusions are solely drawn from their values. For example, stabilities of various materials are frequently compared on the basis of activation energy. The figure below illustrates that such approach is incorrect.

Which process is more rapid?

Apart from the activation energy, the temperature and value of the preexponential factor must be considered. Here, the **high-E** process is fast at high temperatures, where the measurements were done. However, at lower temperatures, both **low-E** processes are faster.
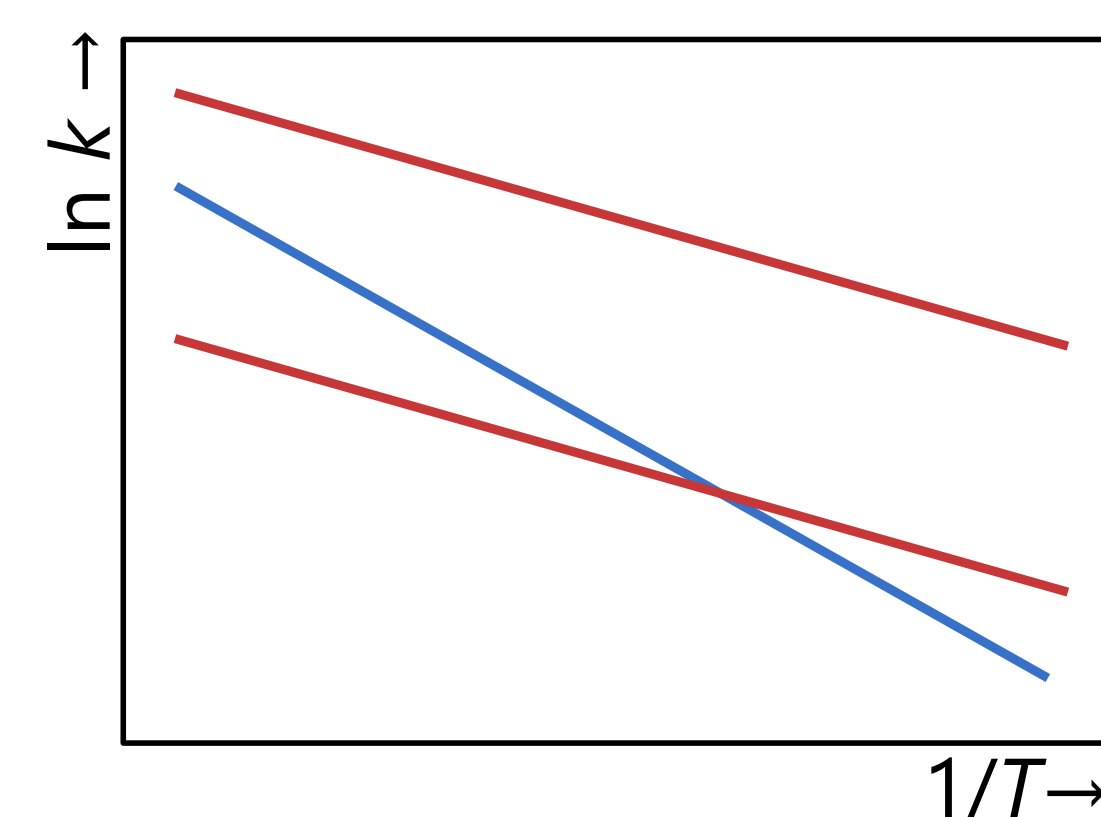
▼ Remedy?

- Correct interpretation of the results: **no conclusion should be drawn from the values of a single kinetic parameter**
- Particular case: **no conclusions should be drawn just from the values of activation energy**

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