2nd Chemiluminescence Symposium

Tuesday November 20th 2007
Berne University of Applied Sciences, Burgdorf, Switzerland

ANALYSIS OF CHEMILUMINESCENCE TRACES

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Analysis of CL traces

Is it possible

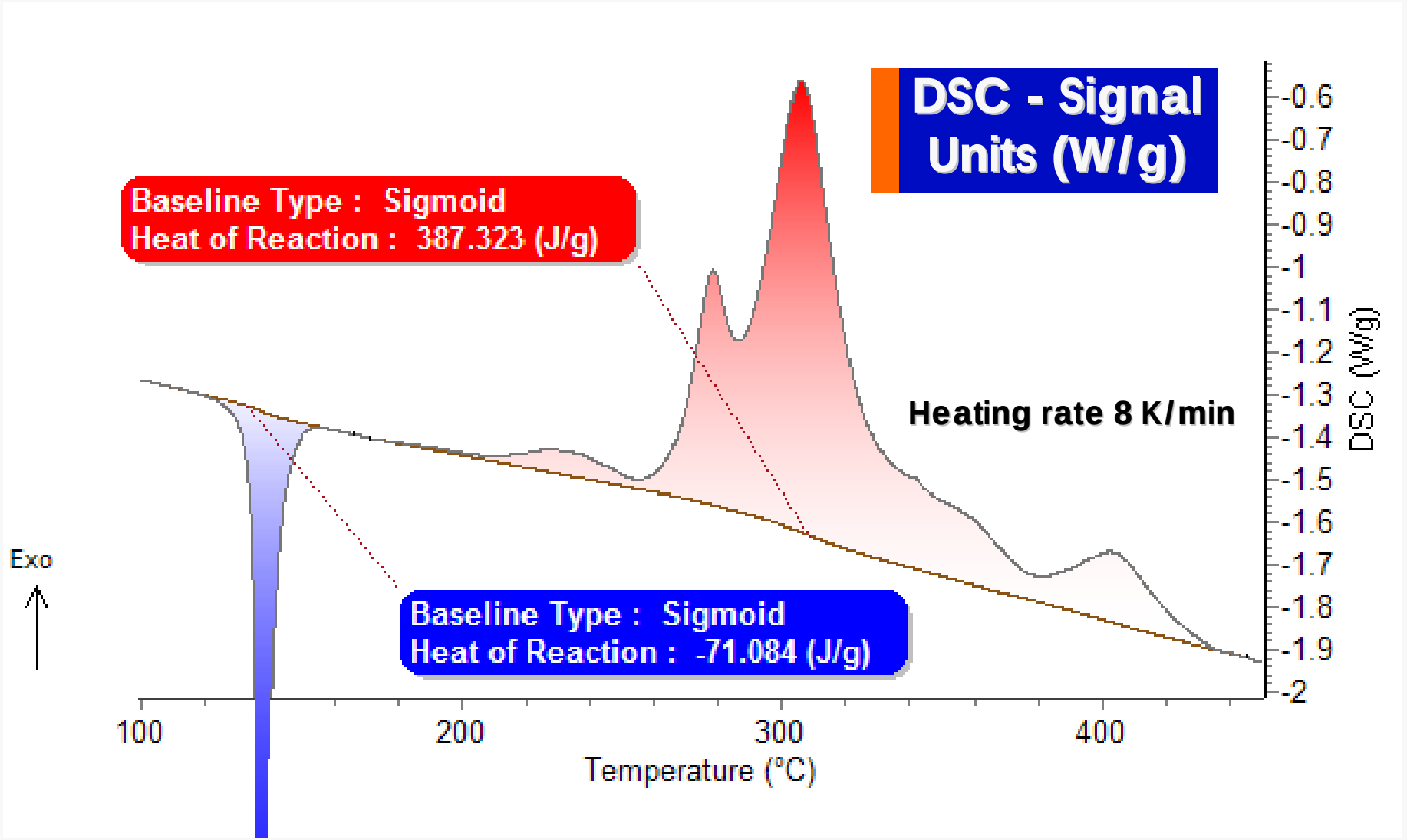
with few chemiluminensce experiments

(mg-scale)

to describe the properties of investigated materials under…

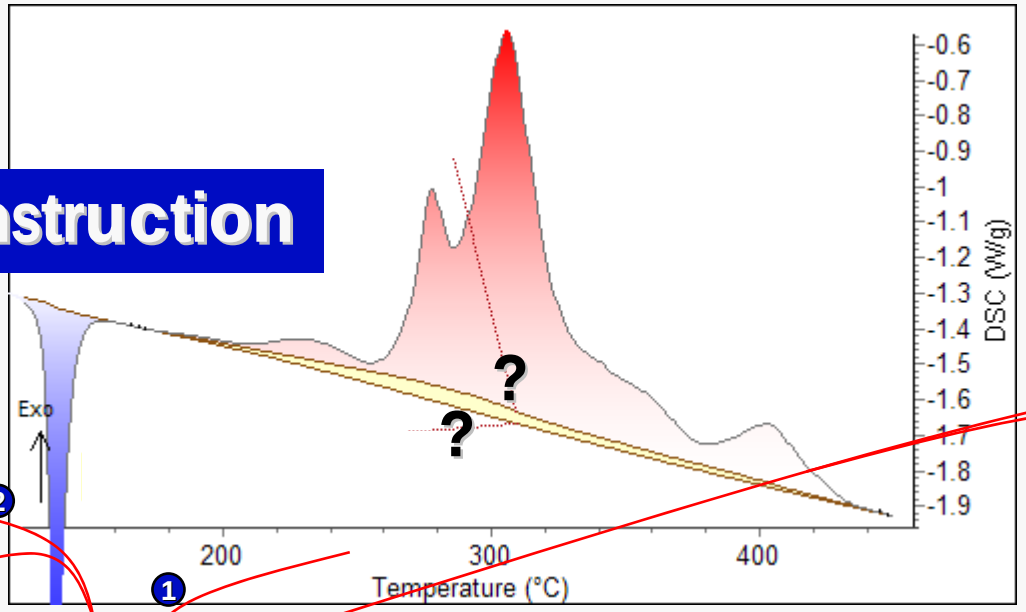
Any temperature profile ?
Lifetime,…
(mg-scale)

Determination of the baseline on DSC traces



Determination of the baseline on DSC traces

Baseline construction



$$\frac{d\alpha}{dt} = \frac{(S(t) - B(t))}{\int_{to}^{tend} (S(t) - B(t))dt}$$

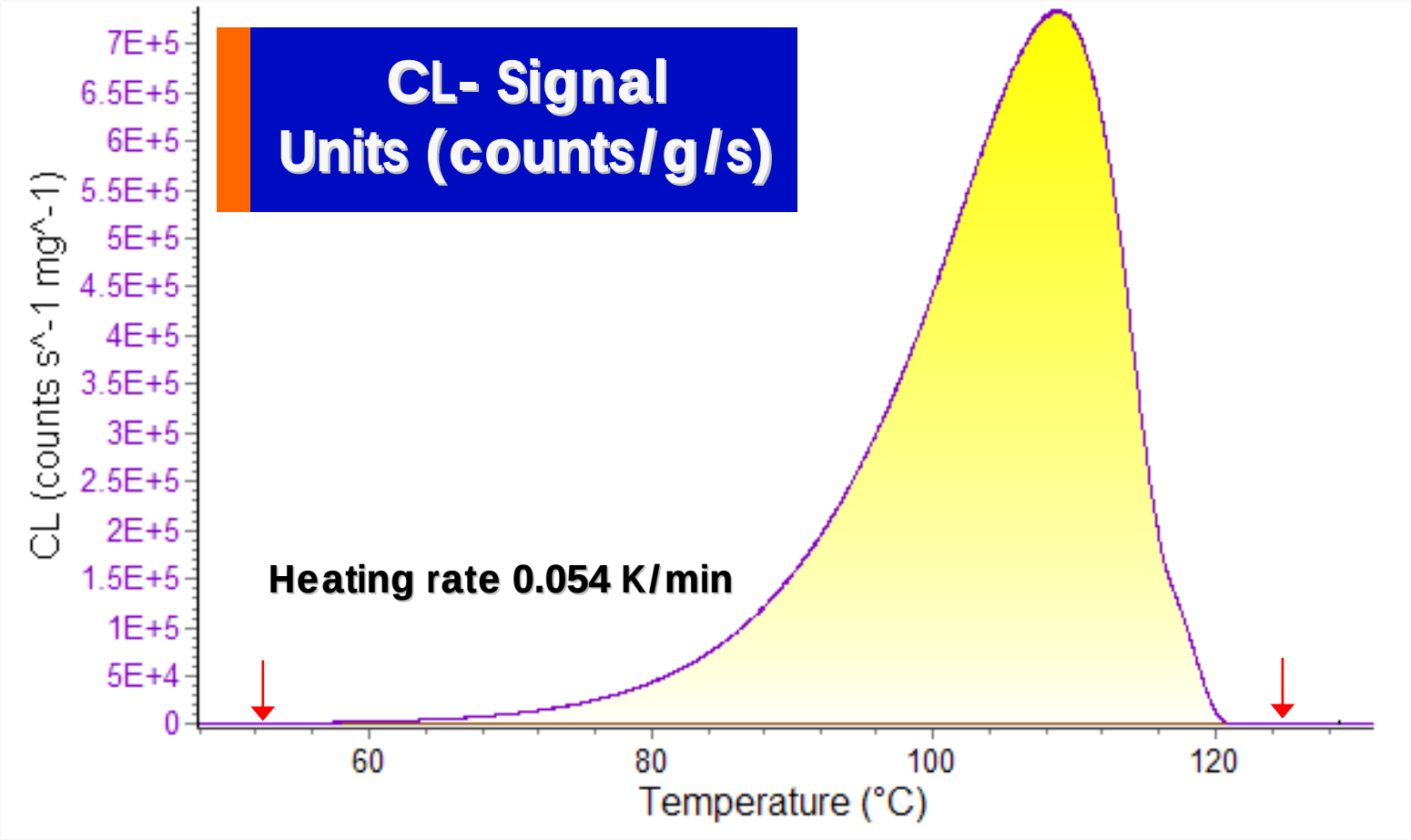
$$B(t) = (1 - \alpha(t)) * (a_1 + b_1 * t) + \alpha(t) * (a_2 + b_2 * t)$$

$$\alpha(t) = \frac{\int_{to}^{t} (S(t) - B(t))dt}{\int_{to}^{tend} (S(t) - B(t))dt}$$

Kinetic parameters

Application of DSC:
The integration of heat flow signal is unfortunately influenced by the course of the baseline.

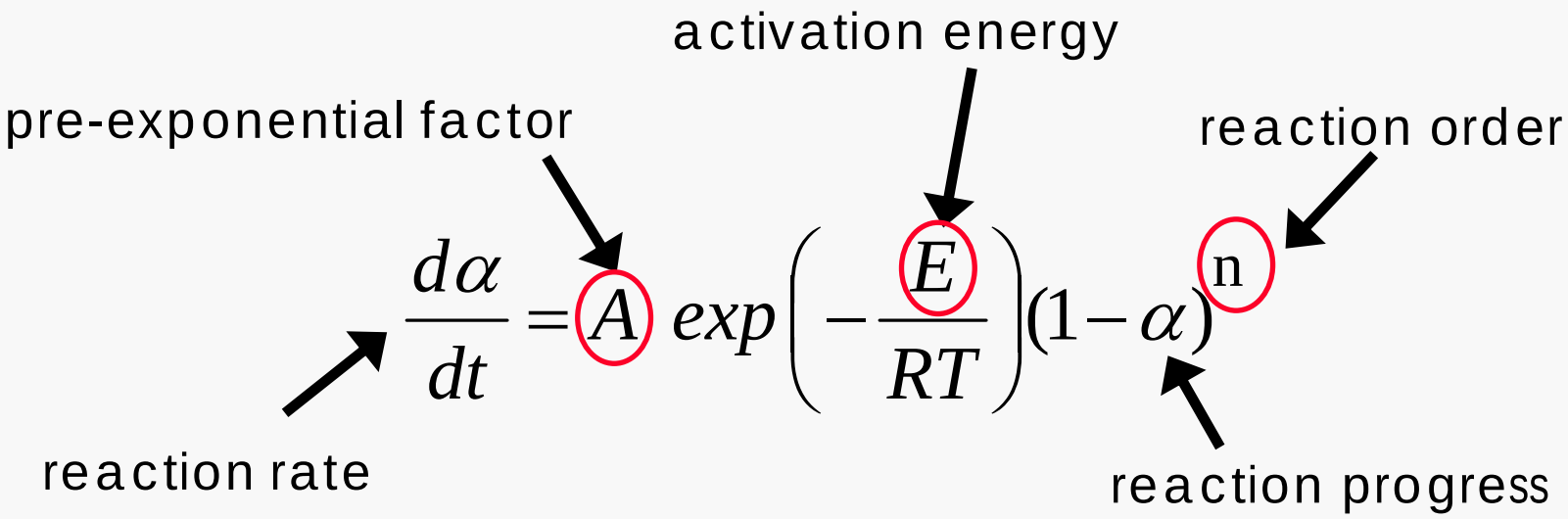
Determination of the baseline on CL traces



Application of CL:
The integration of the signal is well defined

Still commonly used simplification:

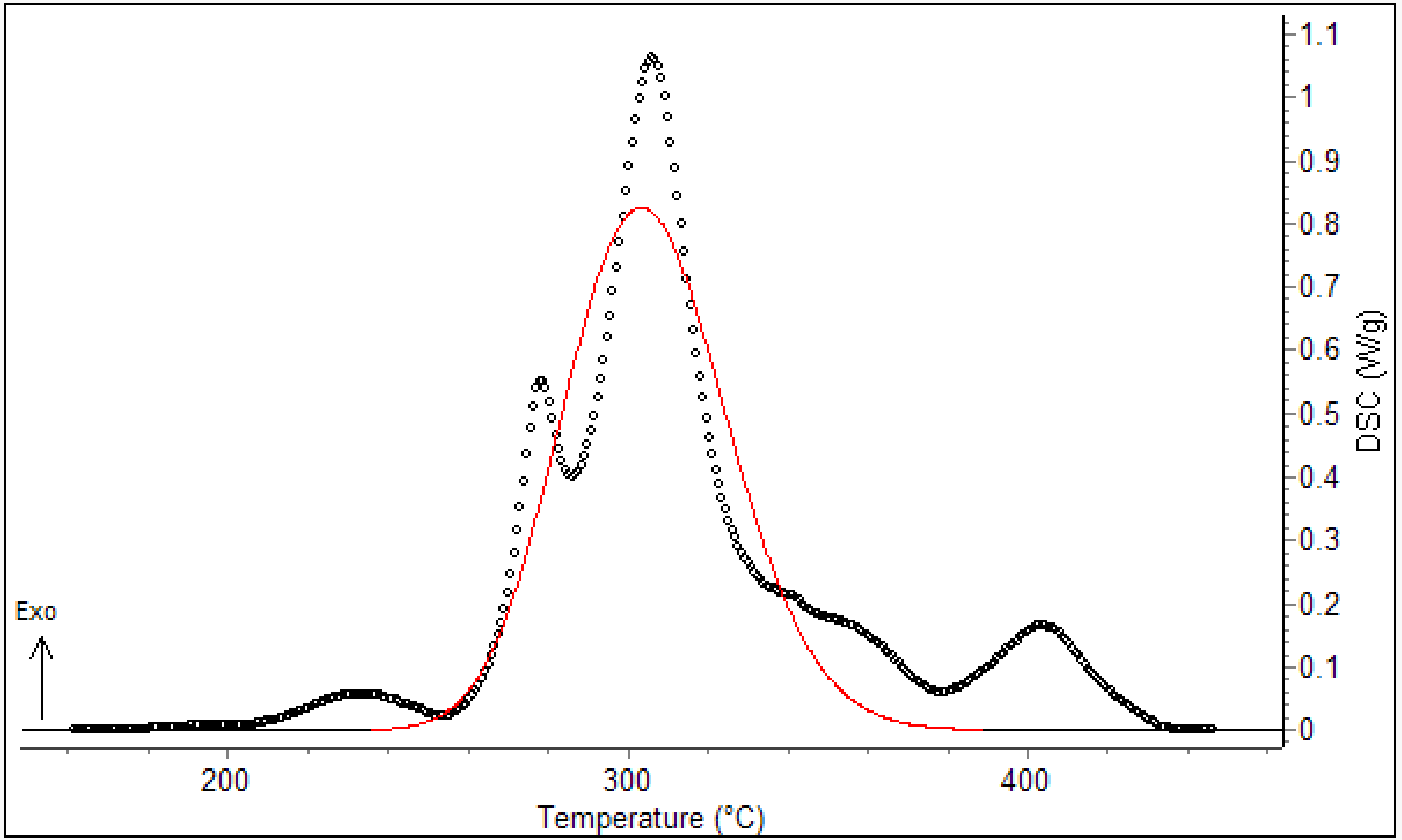
‘ Let‘s assume that the reaction is of n-th order ‘



E = constant
Simplified model f(a) = $(1-a)^n$
Where n-reaction order is assumed to be 0, 1 or 2

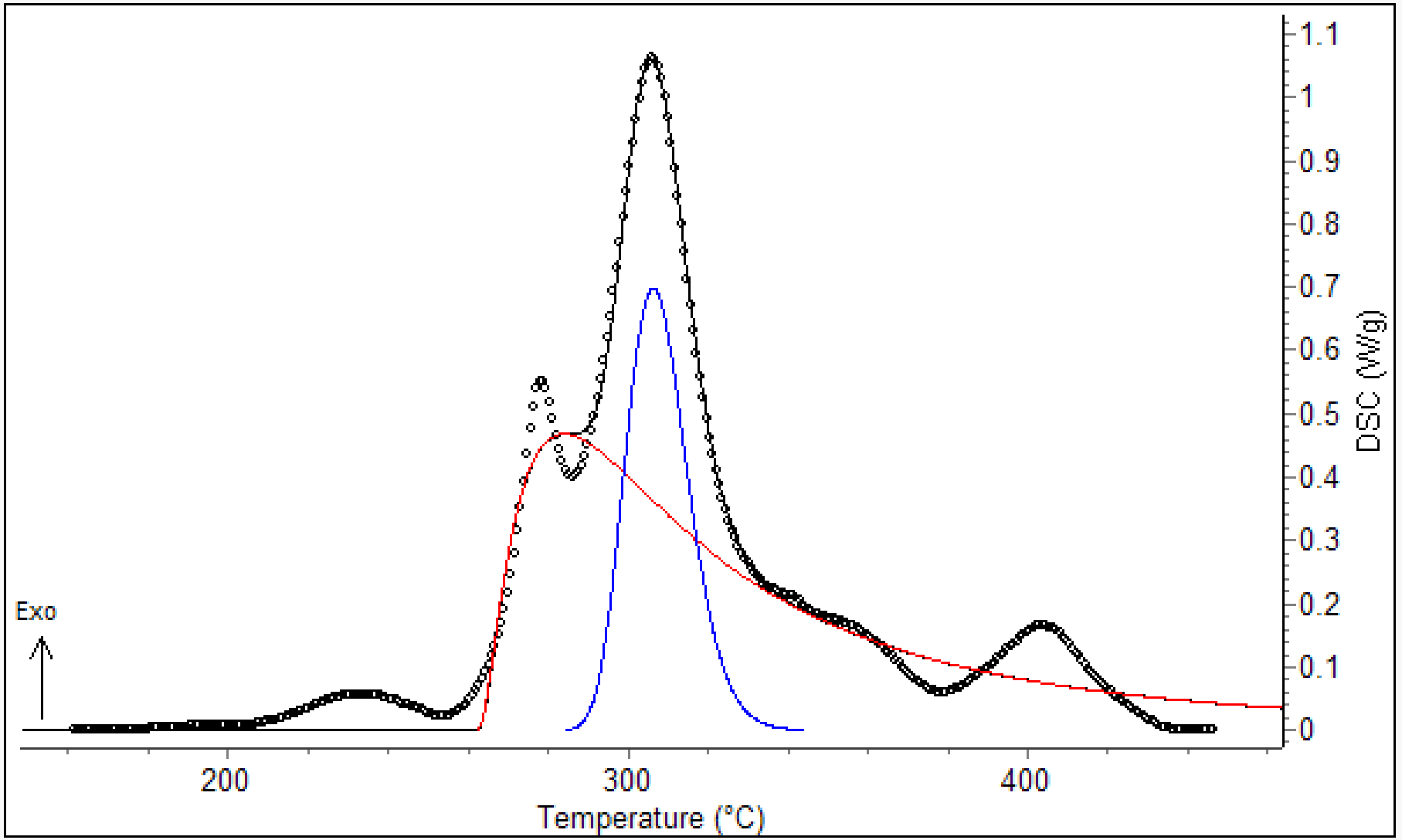
Determination of the kinetic characteristics

A → B



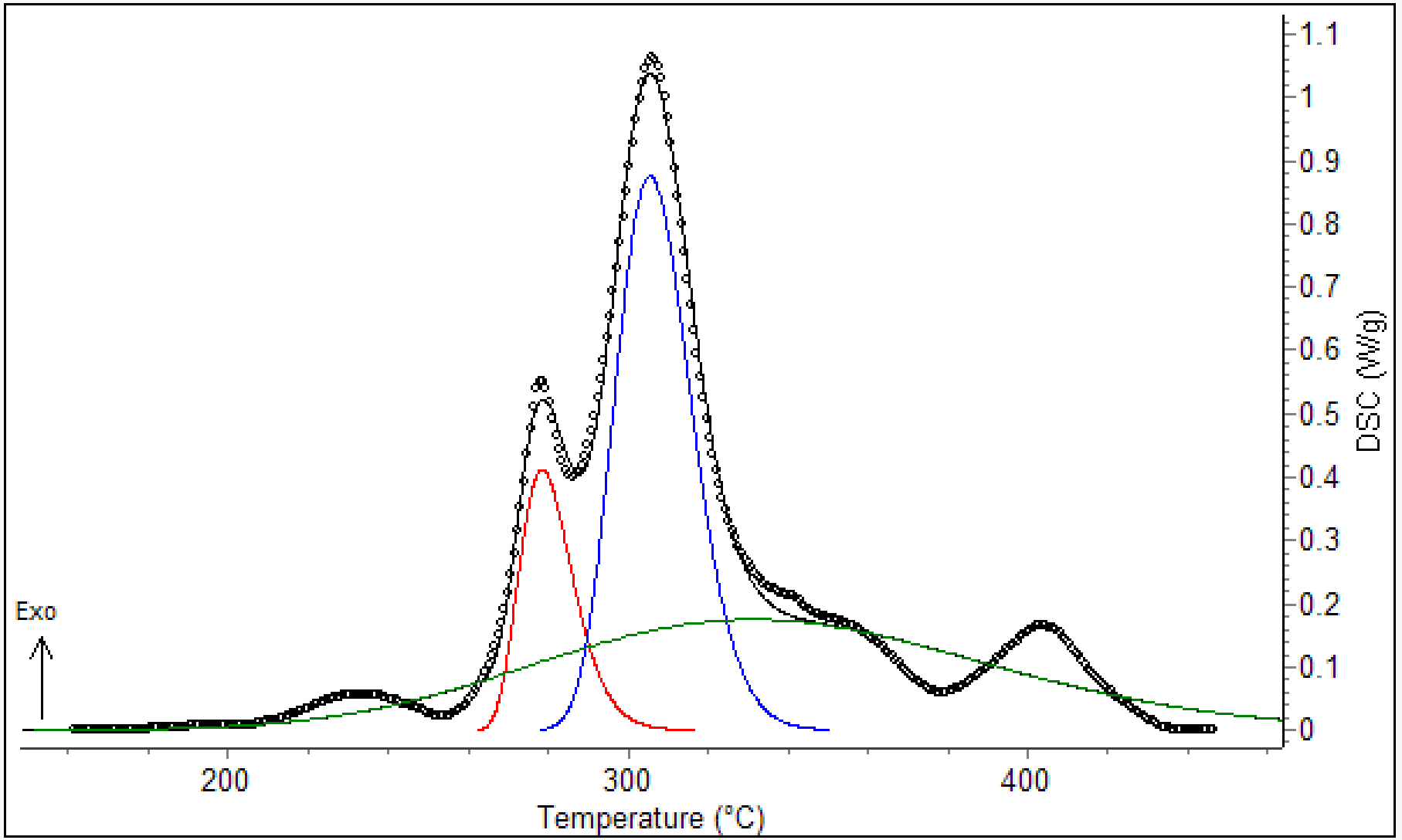
Determination of the kinetic characteristics

A → C → B



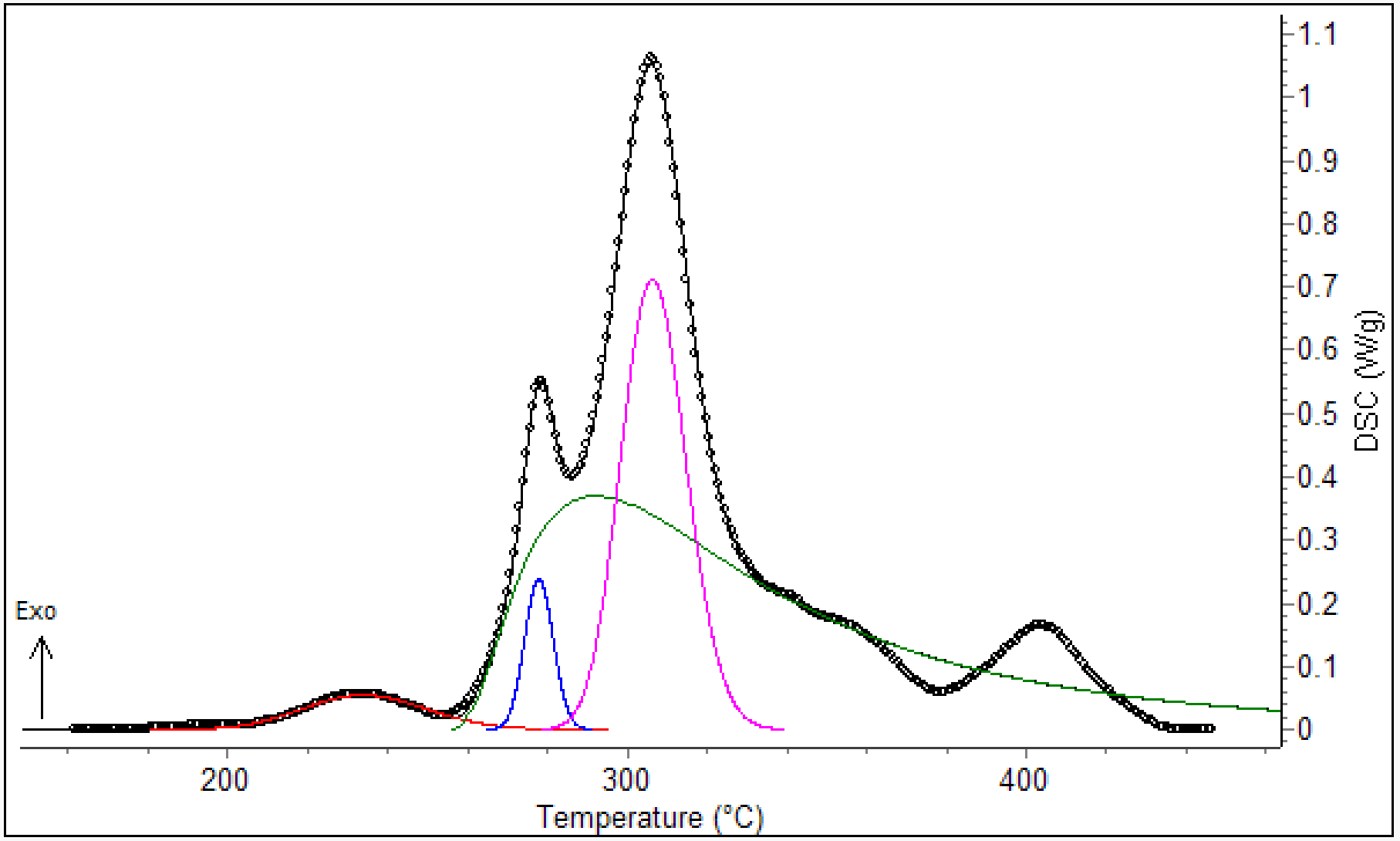
Determination of the kinetic characteristics

A → C → D → B



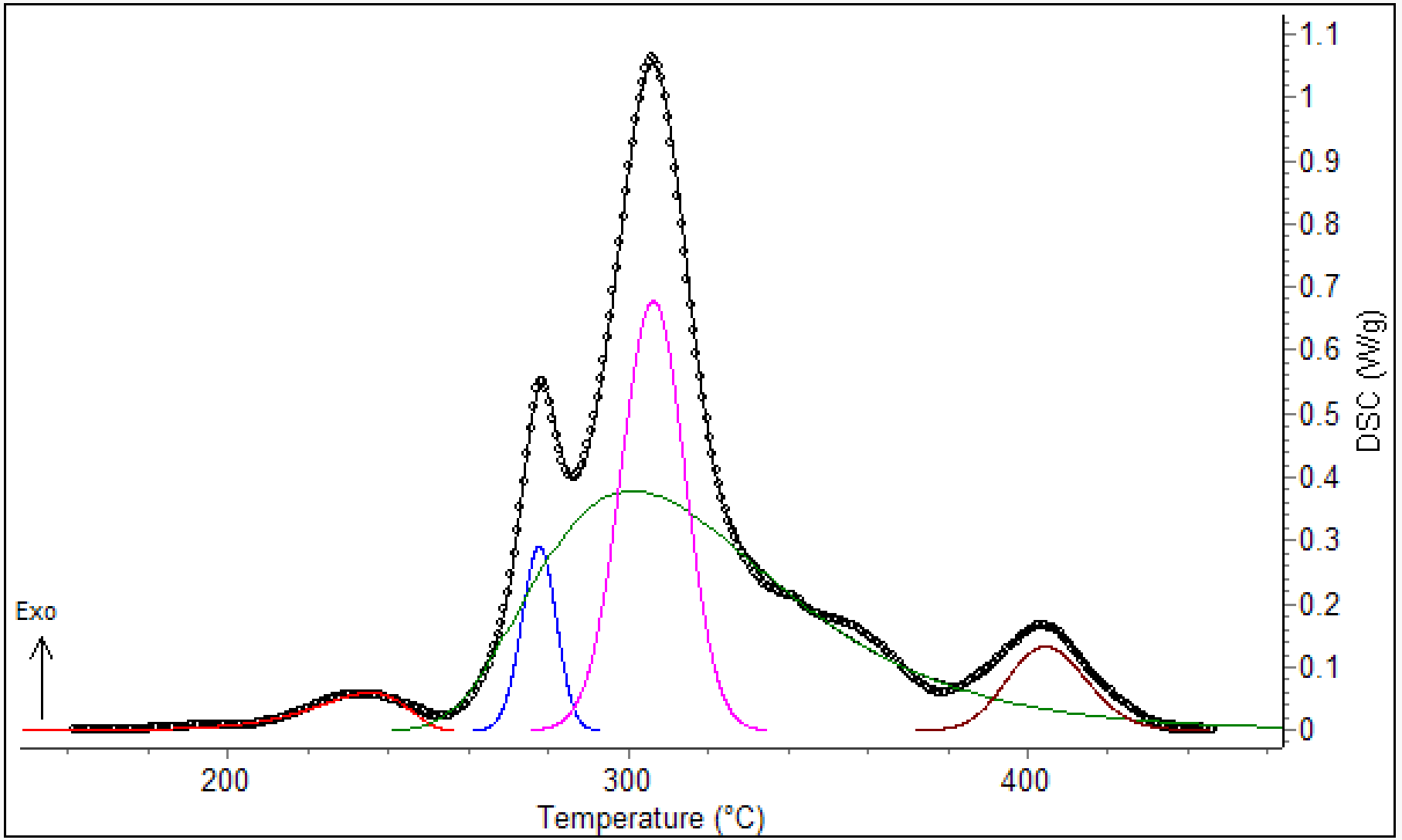
Determination of the kinetic characteristics

A → C → D → E → B



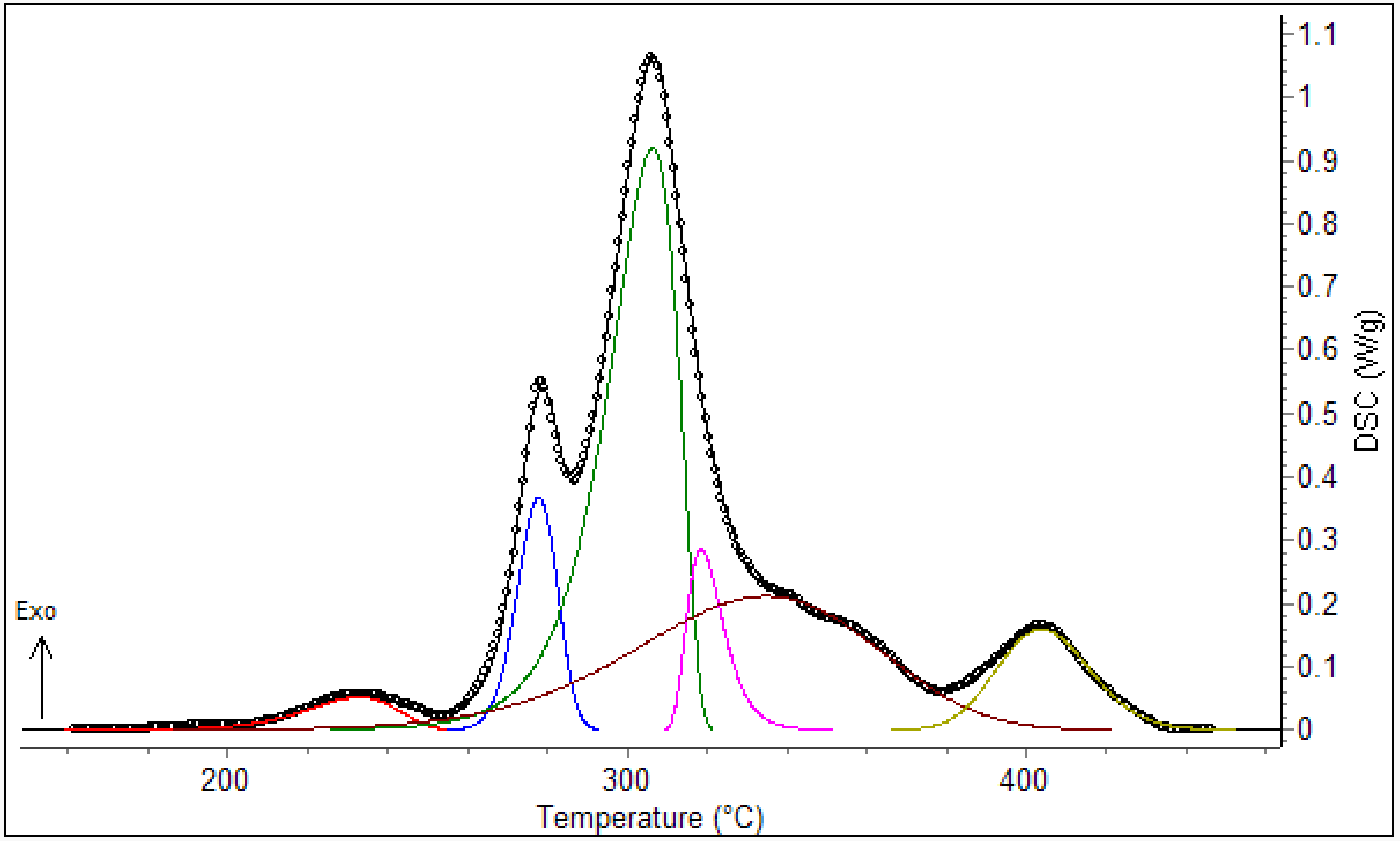
Determination of the kinetic characteristics

A C D E → F → B



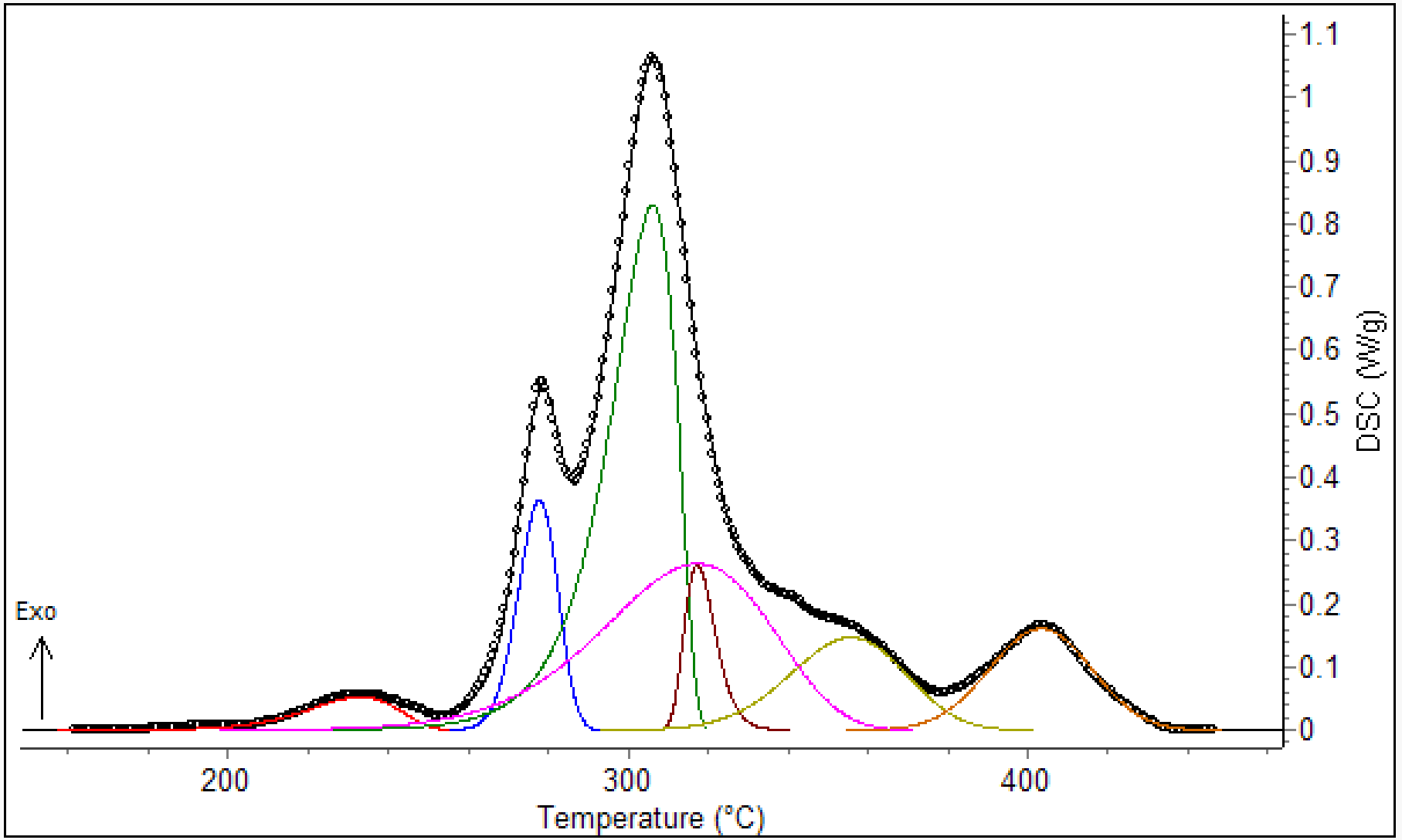
Determination of the kinetic characteristics

A C D E → F → G → B



Determination of the kinetic characteristics

A → C → D → E → F → G → H → B



Determination of the kinetic characteristics

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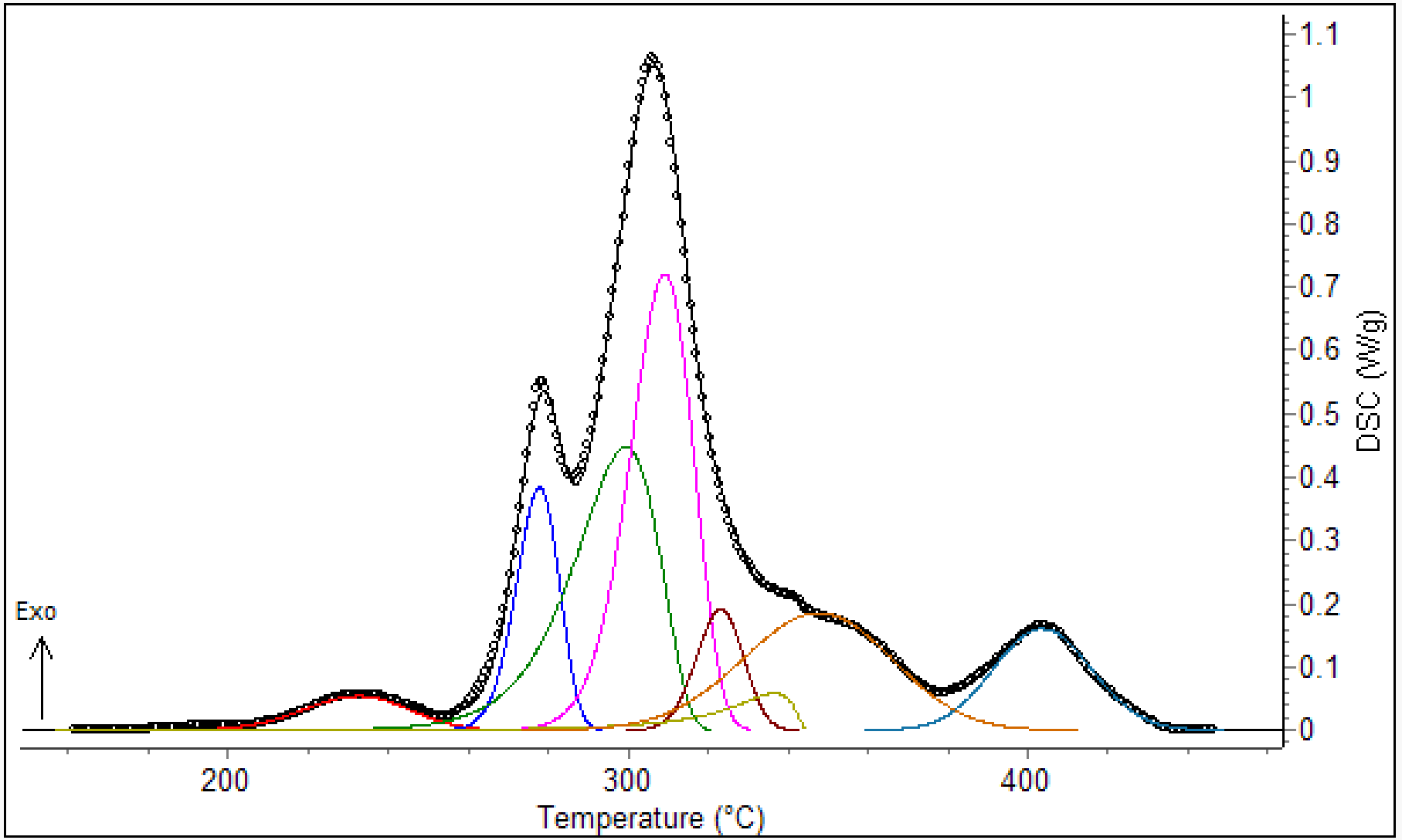

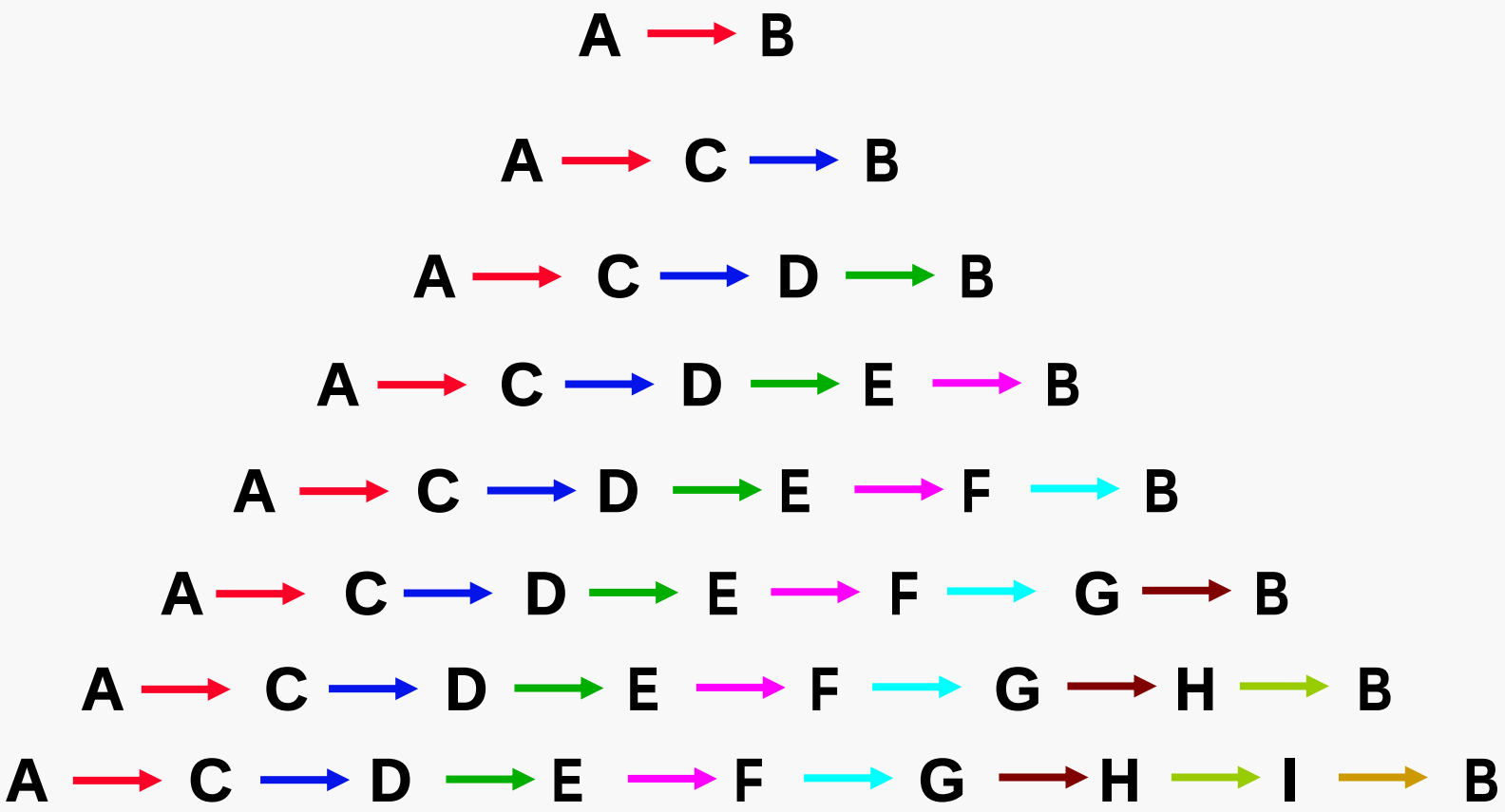
A → B
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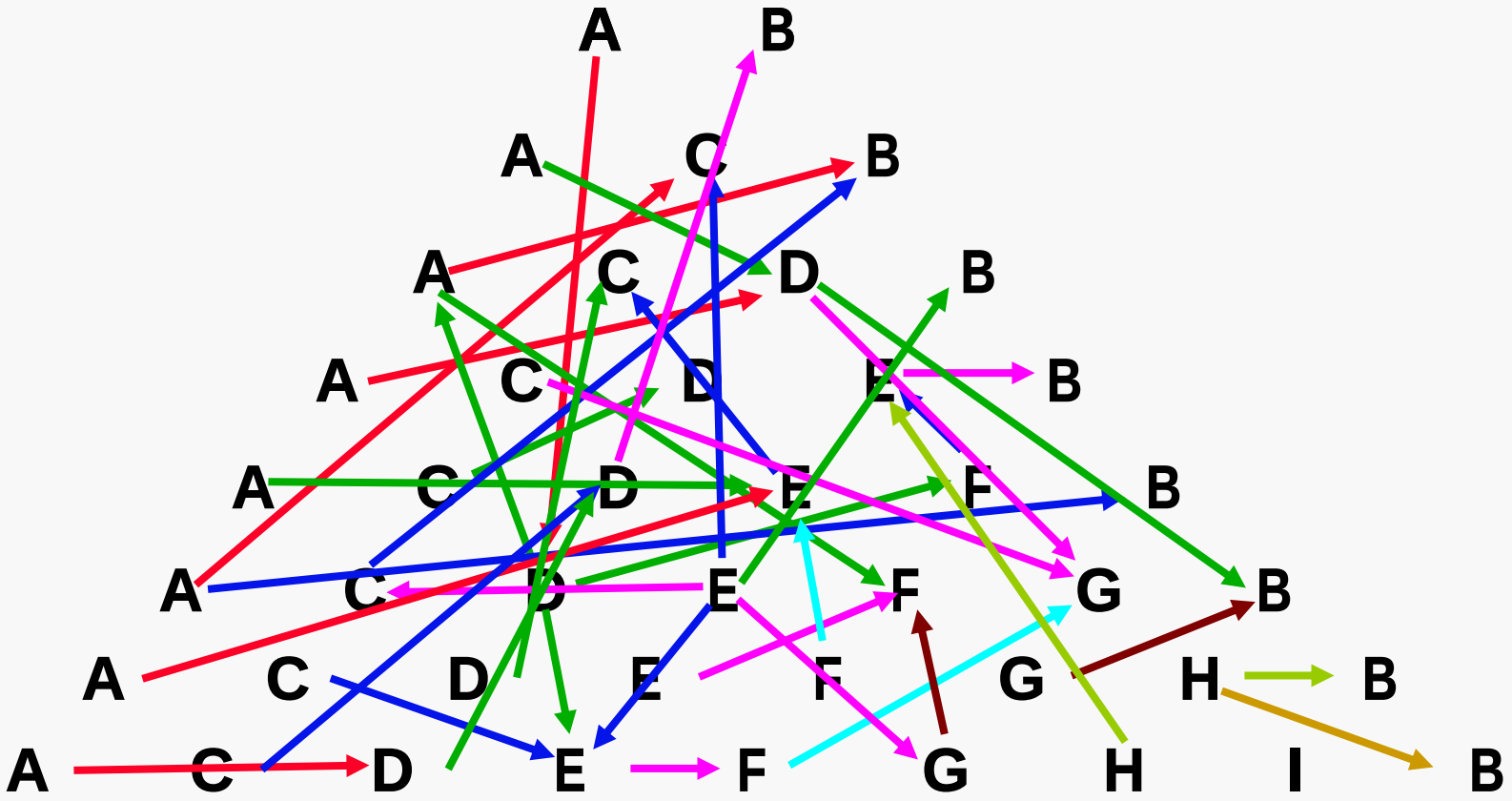
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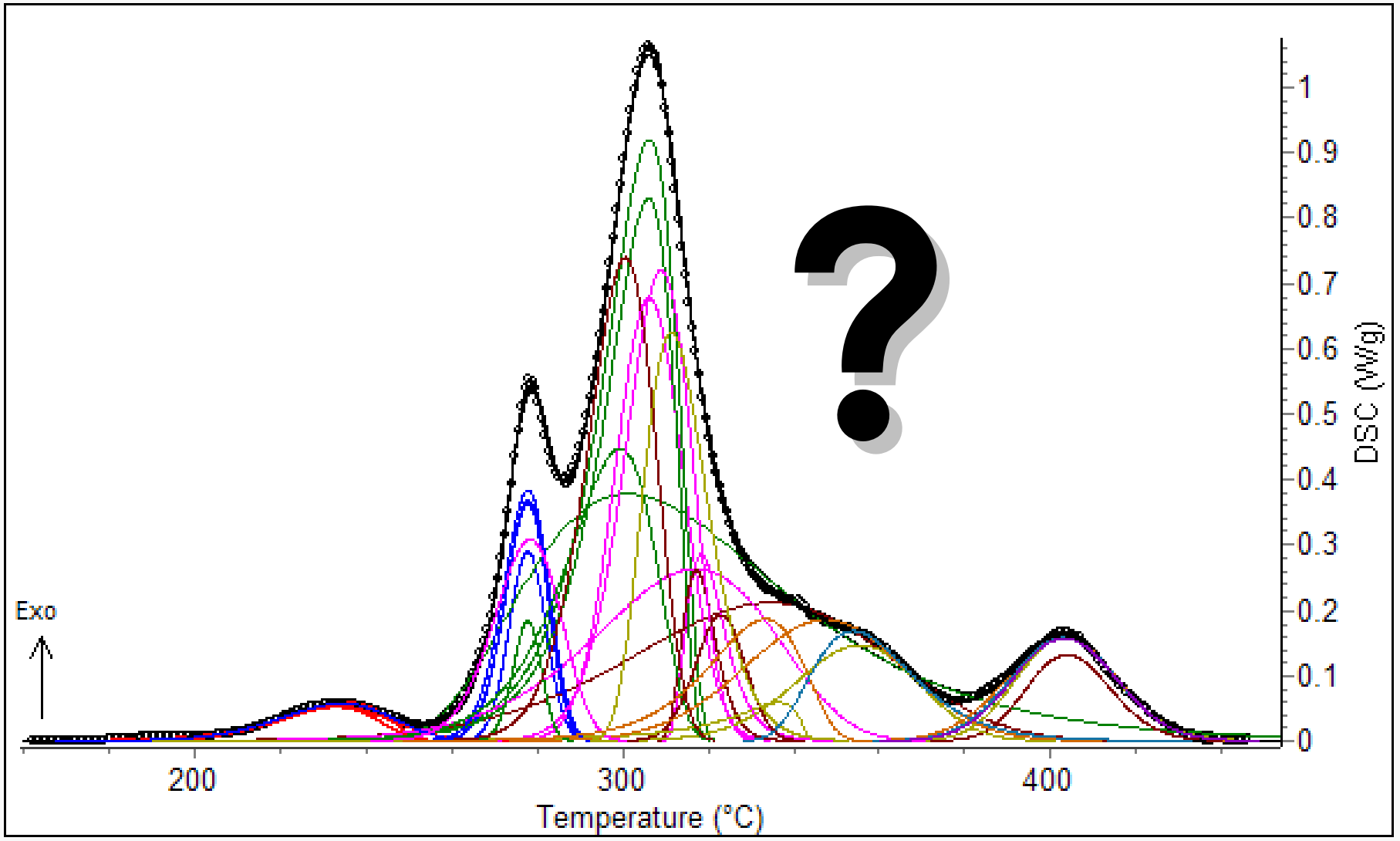
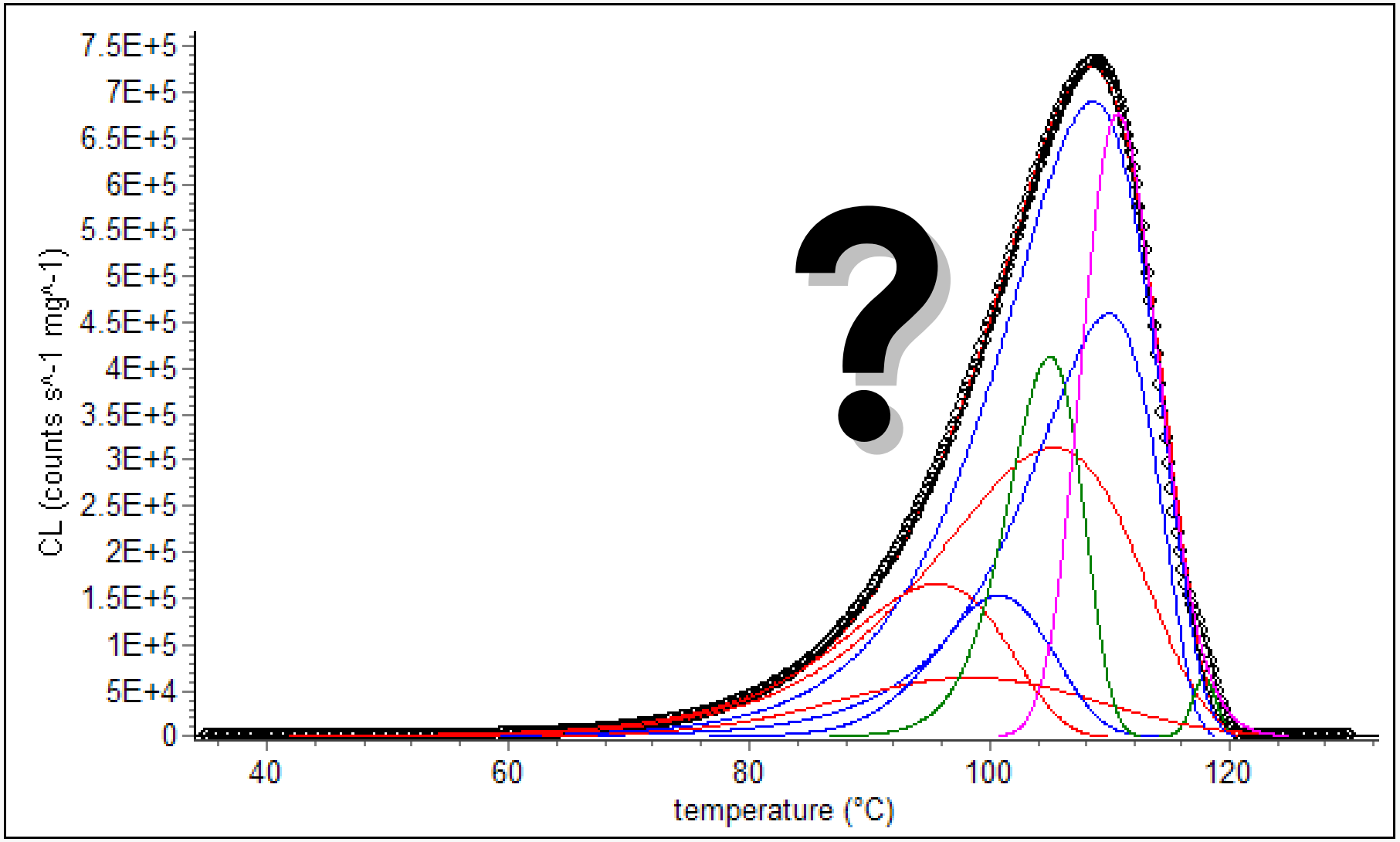
Determination of the kinetic characteristics



Determination of the kinetic characteristics



Determination of the kinetic characteristics

Problem of interpretation of an observation

What do you see ?

- Decomposition reactions very often proceed through multiple stages
- Mechanism of the reactions is generally not known
- Description of the reaction rate by simplified models is very poor

Isoconversional methods are based on the so called isoconversional principle saying that the reaction rate at constant reaction progress α is only a function of temperature.

There are 3 main modifications of isoconversional method:
- Differential (Friedman)
- Integral (Flynn-Ozawa-Wall)
- Advanced integral based on non-linear procedure (Vyazovkin)

Differential isoconversional method of Friedman

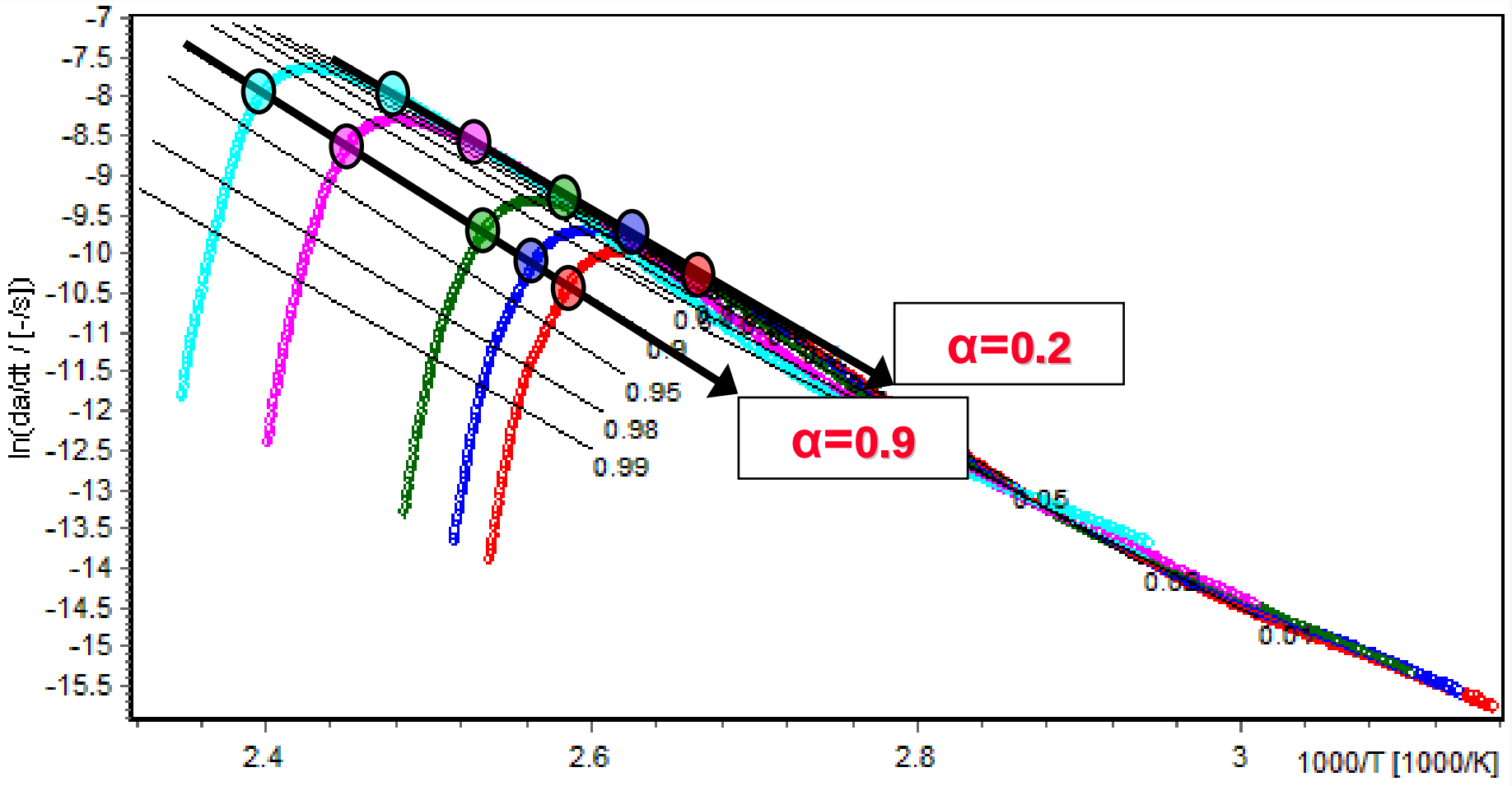
Rate of the reaction is expressed by the Arrhenius equation

$$\frac{d\alpha}{dt} = A \ exp\left(-\frac{E}{RT}\right) f(\alpha)$$

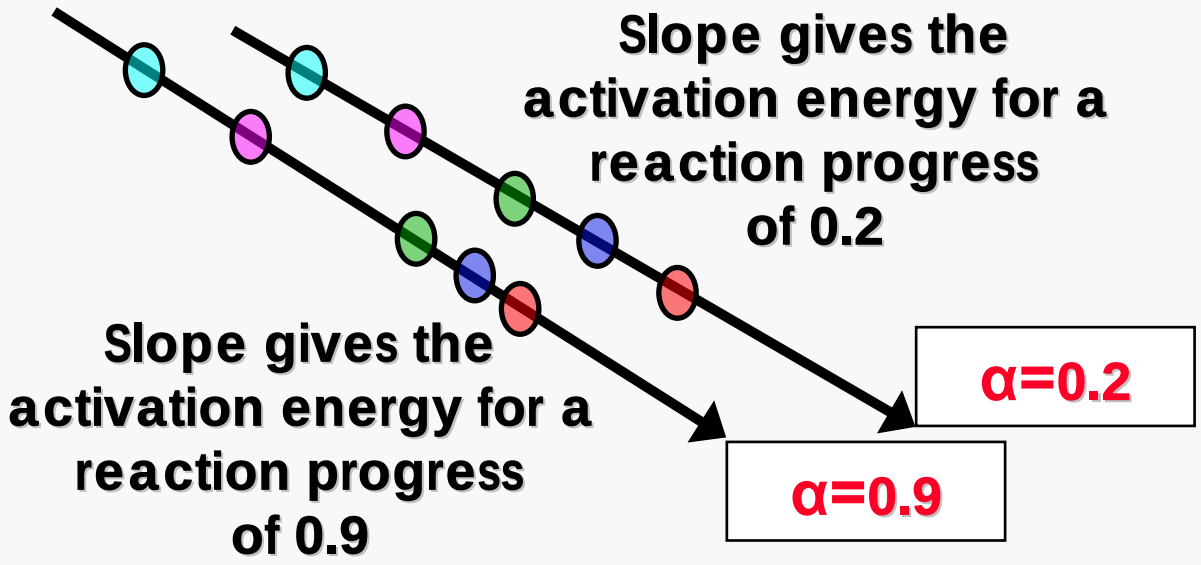
$$\left[\ln\left(\frac{d\alpha}{dt}\right)_{\alpha}\right] = Const - \frac{E_{\alpha}}{R}\left[\frac{1}{T}\right]$$

Reaction rate (Ln) as a function of 1/T at different heating rates

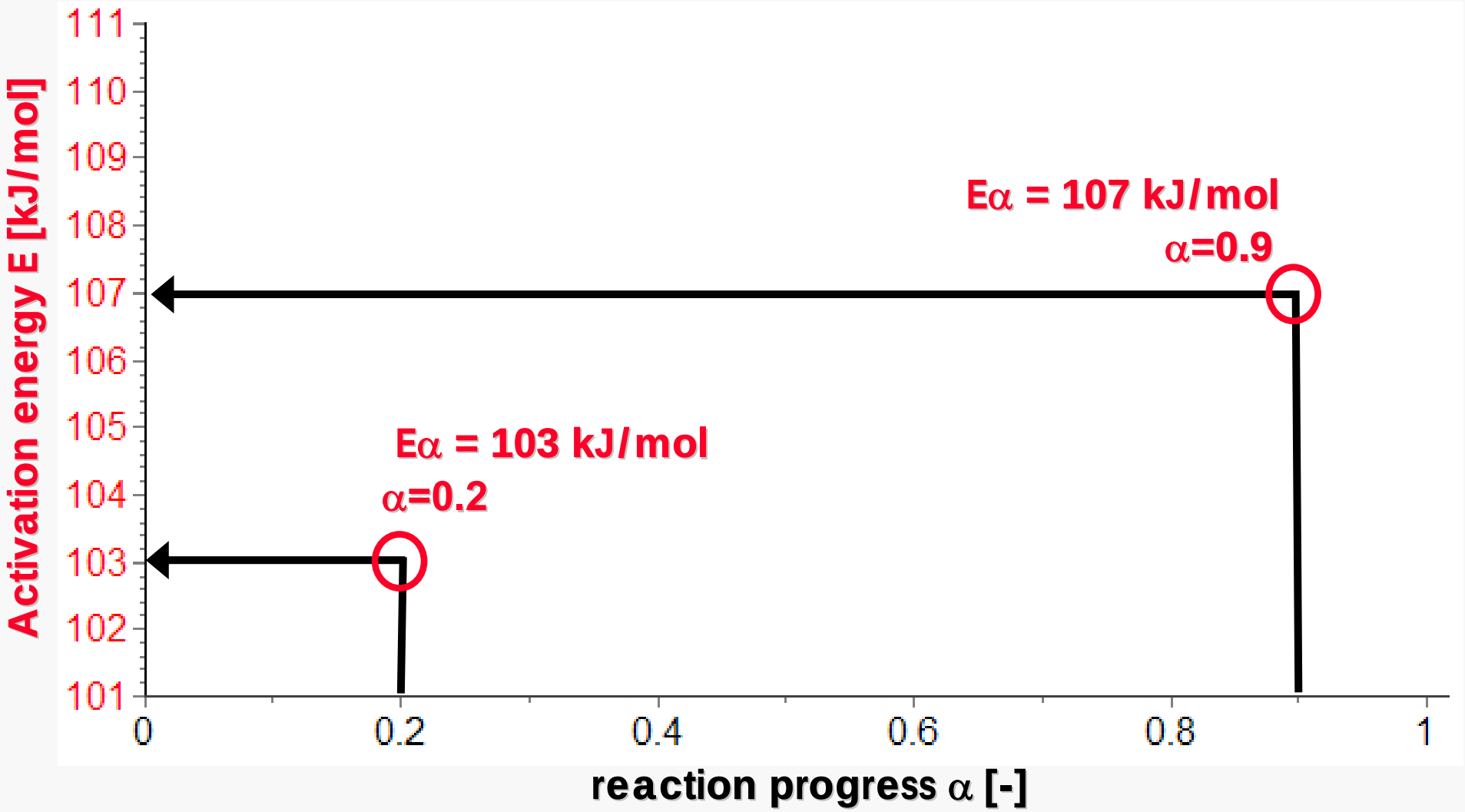
Isoconversional differential Friedman analysis. The slopes of the lines drawn through isoconversional points for certain reaction progress α at different heating rates enable the determination of the activation energy E



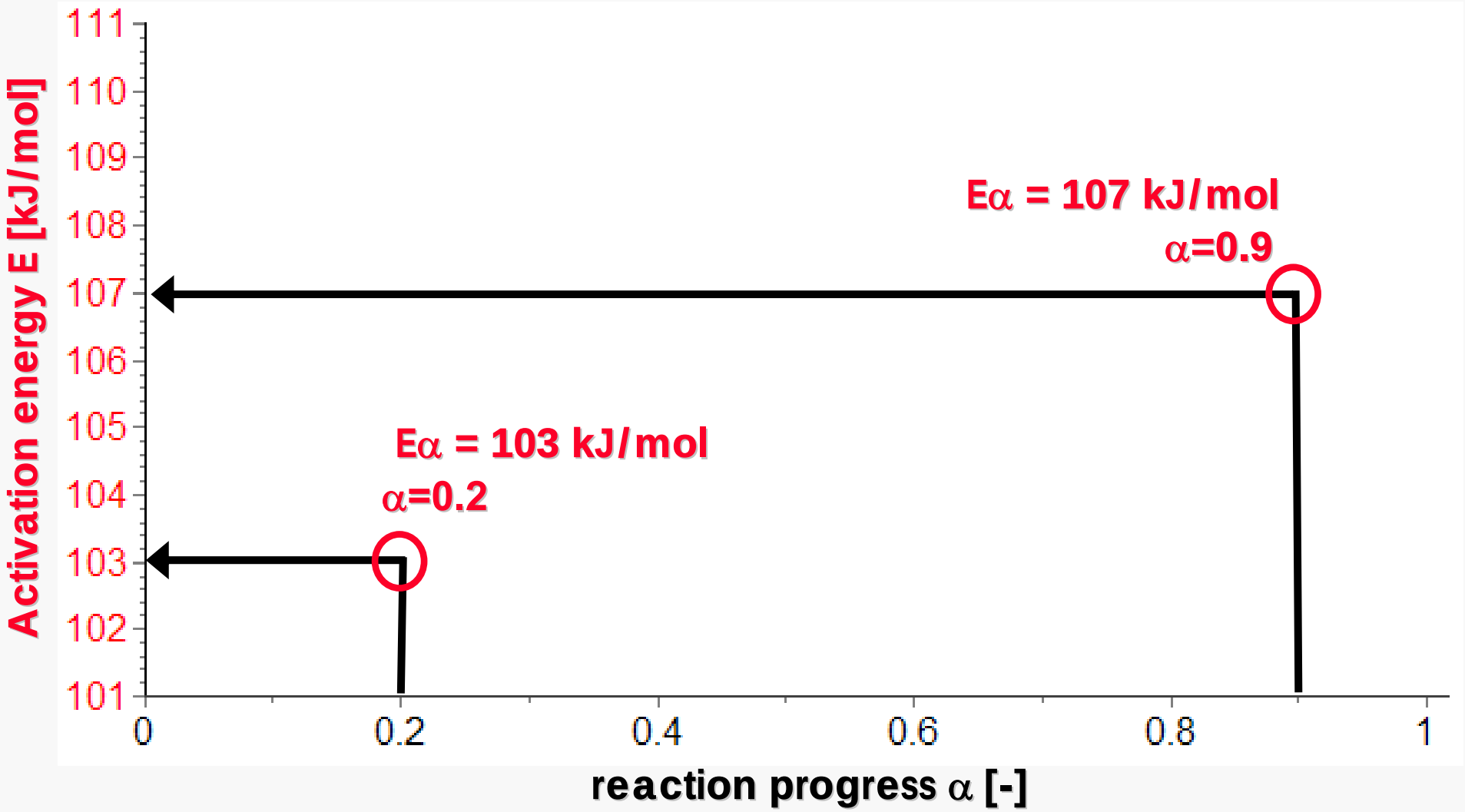
Reaction rates (Ln) for α = 0.2 and α =0.9 as a function of the reverse temperature (1/T) at different heating rates



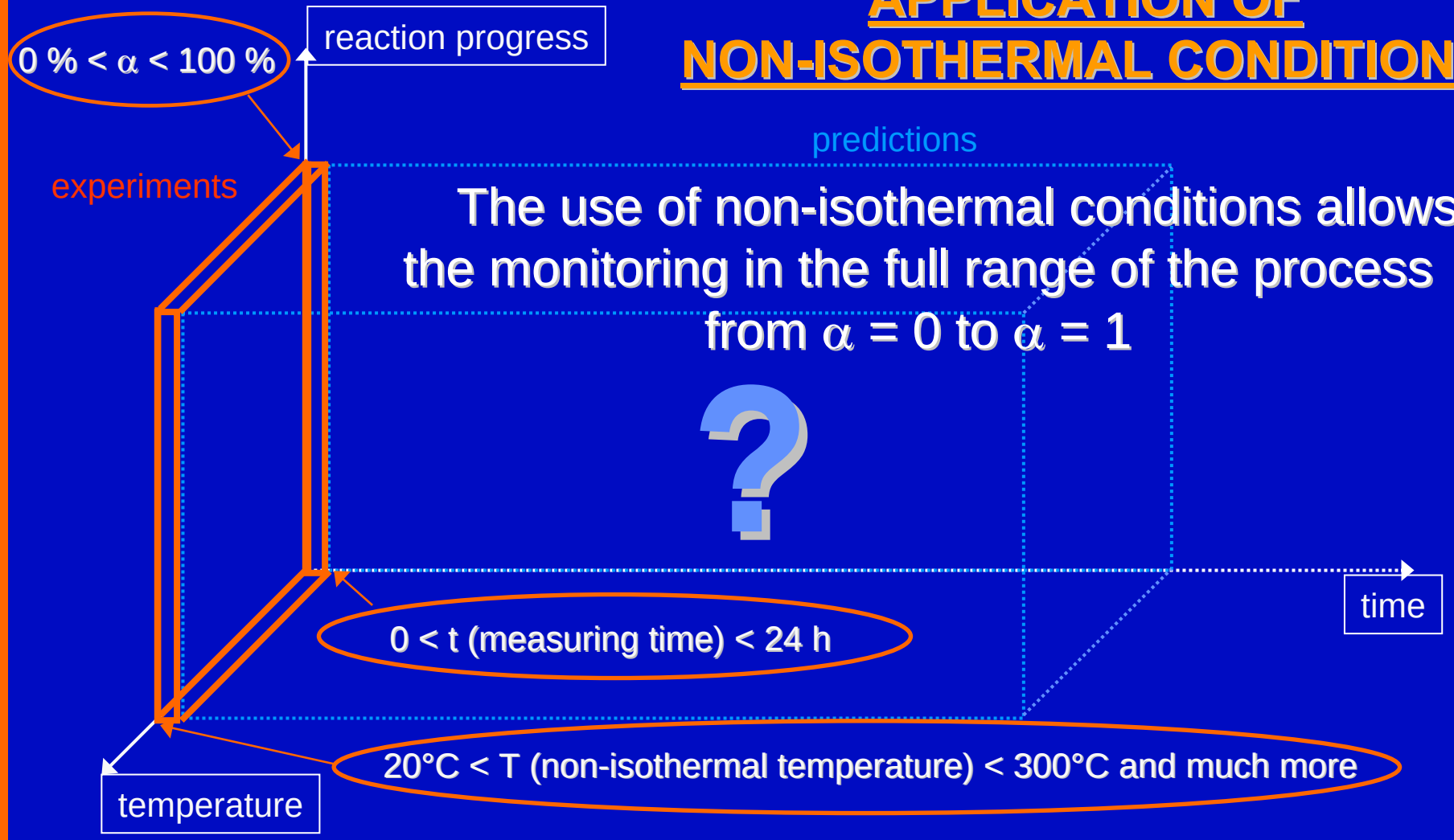
Activation energy E as a function of the reaction progress α



Activation energy E as a function of the reaction progress α



APPLICATION OF NON-ISOTHERMAL CONDITIONS

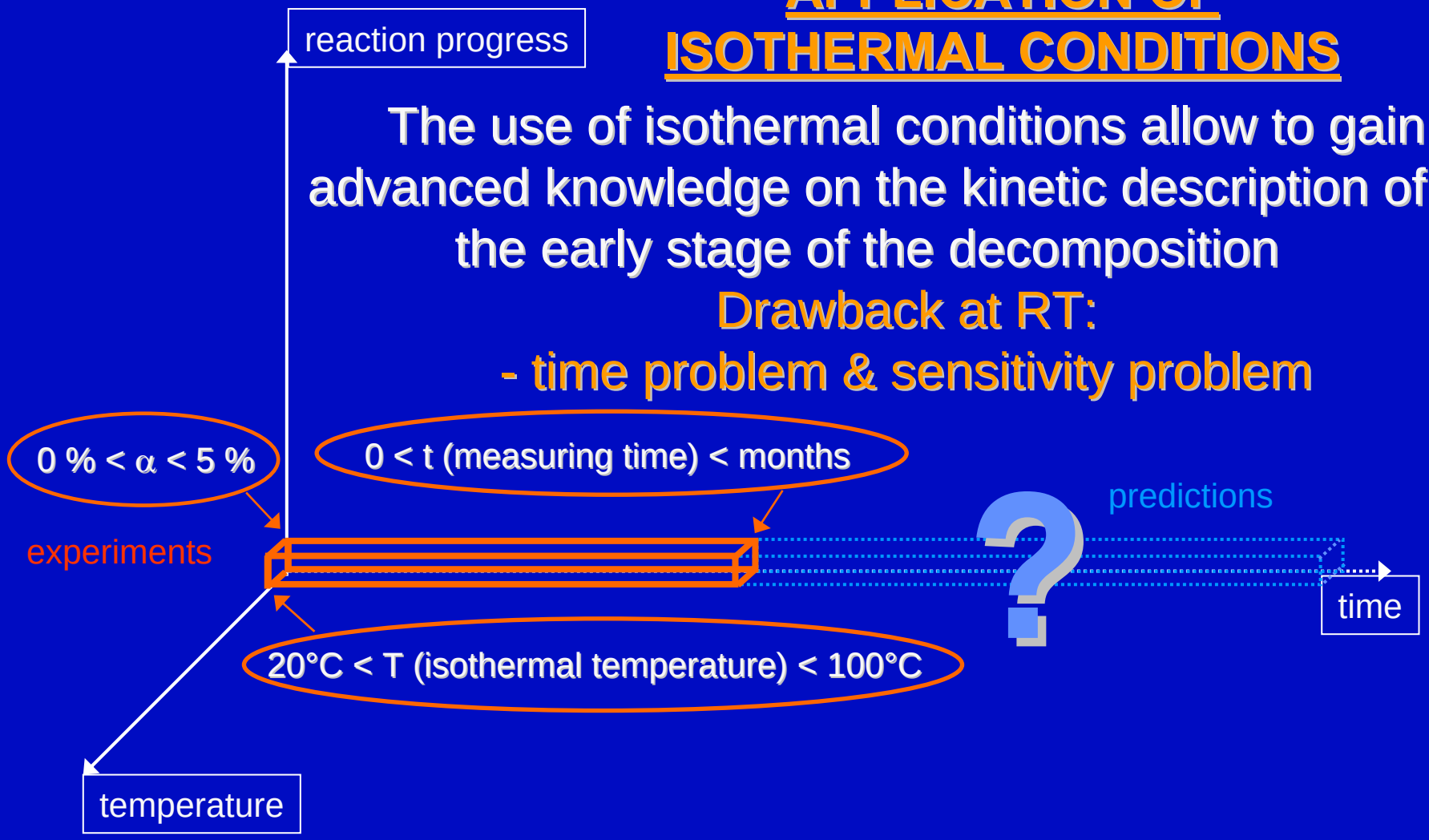


APPLICATION OF ISOTHERMAL CONDITIONS

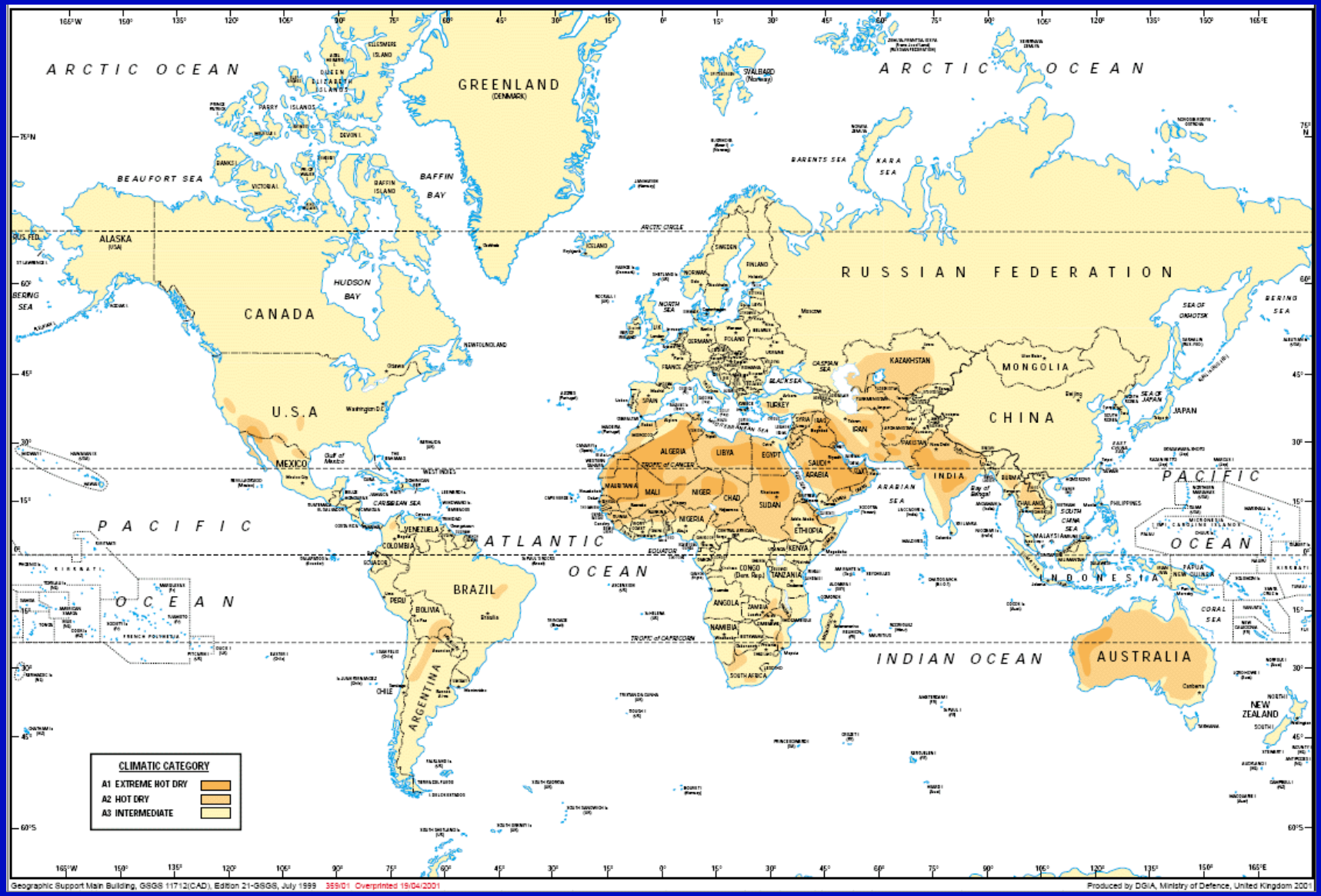
The use of isothermal conditions allow to gain advanced knowledge on the kinetic description of the early stage of the decomposition

Drawback at RT:

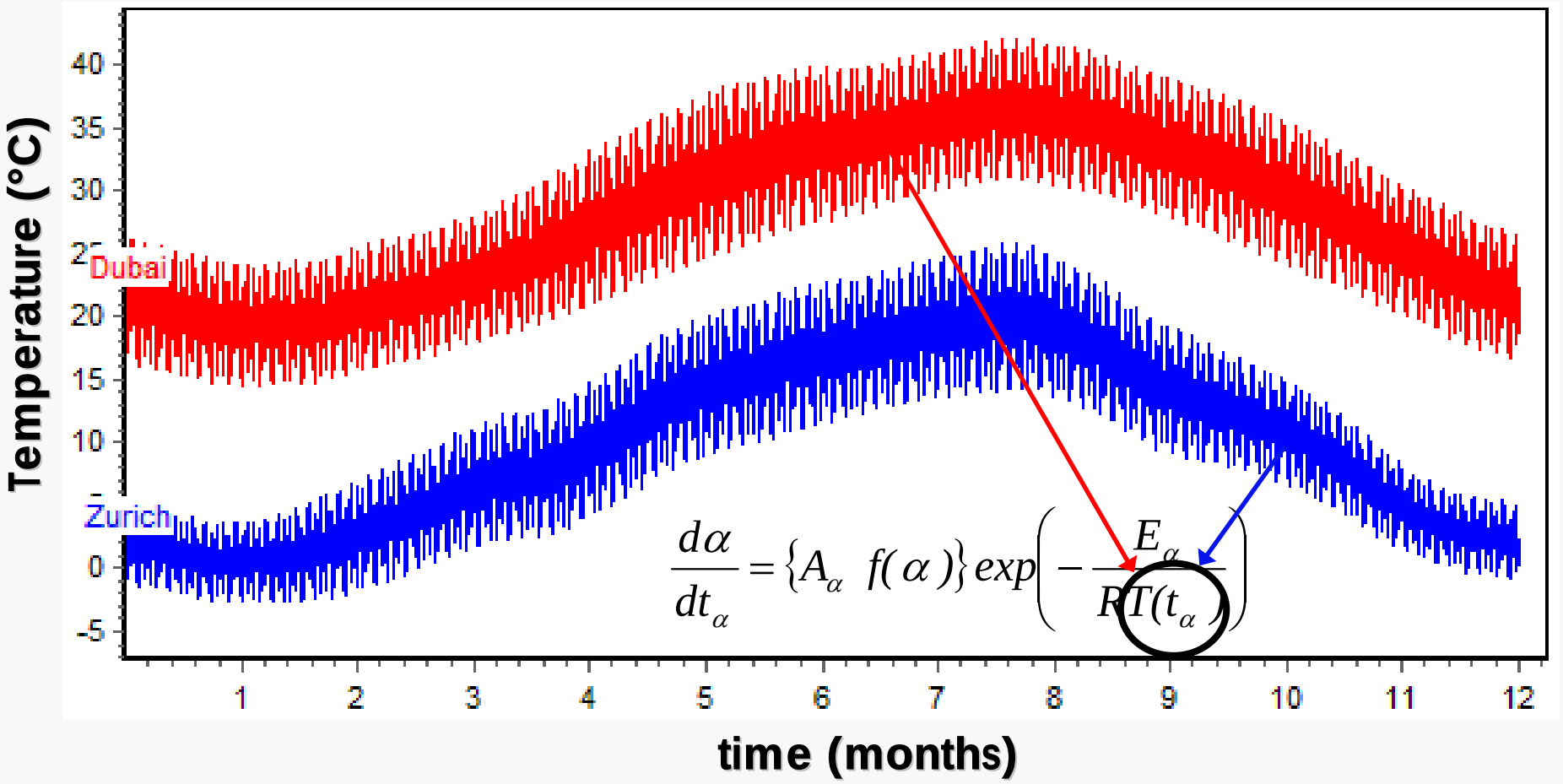
- time problem & sensitivity problem



climatic categories



Summarized temperature cycles world wide for climatic categories
Minimal and maximal diurnal meteorological temperatures recorded during one year

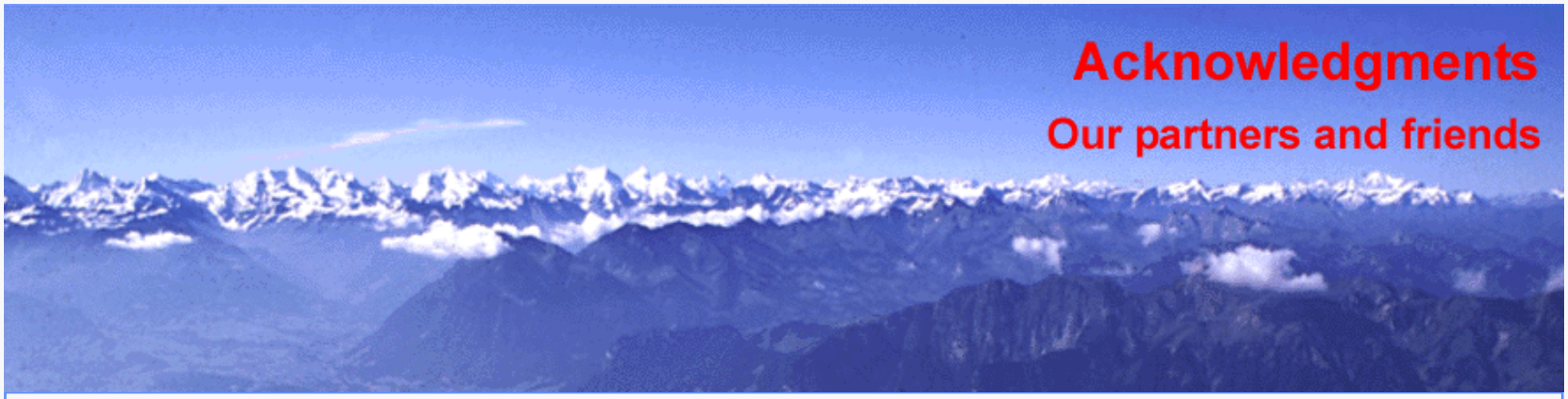


‘Thermal aging through calculations and chemiluminescence’

The correct description of thermal aging applying CL measurements requires the knowledge of two important parameters

(i) the kinetics of the investigated reaction and
(ii) the exact temperature profile.

Both these parameters differently contribute to the reaction progress.



Acknowledgments

Our partners and friends

AKTS AG, C. Borgeat, C. Luyet, L.Xia, JG. Pont, N. Solioz

armasuisse, Dr. P. Folly, B. Berger and J. Mathieu
Swiss Federal office of Public Health, Dr. V. Dudler

Univ. of Western Switzerland, Prof. J.N. Aebischer, S. Gomez, B. Alonso

Swiss Institute of Safety and Security,
Prof. F. Stoessel, Dr. H. Fierz, Dr. P. Reuse

Nitrochemie Wimmis AG, Dr. H. Andres, Dr. M. Ramin, Dr. U. Schädeli, Dr. B. Vogelsanger