Sestak’s key note lectures at
34th NATAS Conference in Bowling Green, USA, 2006 &
1st CEEC-TAC1 conference in Craiova, Rumania 2011
Rationale and Fallacy of Thermoanalytical Kinetics
Gradual birth of the idea of thermal analysis

Heat as an instrumental reagent

Thermodynamics
- temperature
  - latent heat
    - Black
  - thermometry, calorimetry
    - Sadi Carnot
    - Clapeyron
  - Kelvin
  - temperature gradients
    - Newton
  - heat conductivity
    - Fourier

Kinetics
- workless dissipation
  - Stokes
  - Planck
- dissipationless work
  - Maxwell
  - Clausius

thermodynamics
- thermomechanics
  - Gibbs
  - Boltzmann
  - Kirchhoff
  - Onsager

thermostatics
- thermodyn. statistics
  - Landau
  - Noll
  - Coleman
  - Ising

rational thermodynamics
- thermodyn. of irreversible proc.
  - Truesdell
  - Prigogine

cooperation
Gradual birth of the field of reaction kinetics

exp(-E/RT)

J.W. Gibbs  S.A. Arrhenius  L.E. Boltzmann  I. Prigogine
V. Šatava  E. Segal  T. Ozawa  J.H. Flynn

Ongoing formation of non-isothermal kinetics

P.D. Garn  D. Dollimore
Dedicated to the 40th Anniversary of Ozawa-Flynn iso-conversional kinetic evaluation method.

T. Ozawa: “A new method of analyzing thermogravimetric data”

Polymer Letters B4 (1966) 323

Details see e.g.: P. Šimon, “Iso-conversional Methods: fundamentals, meaning and application”
Comprehensive treatise on non-isothermal kinetics:


⇒ E. Segal, F. Fatu “Introduction to non-isothermal kinetics”, Romanian Academy, Bucharest 1983


Lecture objectives seeing erroneous beliefs:

Detailed inspection of kinetic analysis by thermal analysis as aimed to the most implicated processes

What is the kinetic equation and degree of conversion

Non-equilibrium background – phase diagrams

Mathematical manipulation with kinetic equation

Fractal-like models of reaction path

Modulated and oscillatory reactions

Interplay of classical and quantum diffusion

Where are the limits of more exhaustive kinetics?
Process specification

Temperature $T_1, T_2 \ldots T_i$
Degrees of conversion $\alpha_1, \alpha_2 \ldots \alpha_i$
$\beta_1, \beta_2 \ldots \beta_i$
etc. . , .,  \ldots .
Equilibrium background $\lambda_{eq}$

Process evolution (time, t)

Temperature change $dT_1/dt, dT_2/dt \ldots dT_i/dt$
Rate of conversion 1 $d\alpha_1/dt, d\alpha_2/dt \ldots d\alpha_i/dt$
Rate of conversion 2 $d\beta_1/dt, d\beta_2/dt \ldots d\beta_i/dt$

Elementary steps involved 1, 2 \ldots \ i
parallel, consecutive, competitive, branching, \ldots
Elementary steps involved 1, 2 ...... i

Homogeneous $T, \alpha, \beta, 1=2=1$

Heterogeneous $T_i, \alpha_i, \beta_i, 1\neq2\neq1$

Traditional simplification: the overall process is represented by single $\alpha$, i.e., other $\alpha`, \beta`s$ are zero or ignored
Controversial character of TA/XRD-bulk & SME-spot observations

averaged curve response

single spotted picture
Invariant and variant processes

Equilibrium background

\[ \lambda = \alpha \lambda_{eq} \]

\( \beta \)-phase separation

Kinetic phase diagrams
\[ \frac{d\alpha}{dt} = \alpha' = f_\alpha (\alpha, T) = k(T) f(\alpha) f(\alpha, T) \]

\[ \frac{dT}{dt} = T' = f_T (\alpha, T) \cong T_0 + f(t)_{outer} + f(t)_{inner} \]

- **Kinetic equation**
- **Self-heating/cooling**
- **T-gradients**
- **Simplification**

\[ f(\alpha, T) = 1 \]
\[ f_T (\alpha, T) = f_T (T) = \phi \]

\[ \frac{d\alpha}{dt} \text{ (reaction rate)} = \alpha' = f_\alpha (\alpha, T) = k(T) f(\alpha) \]

\[ \frac{dT}{dt} = \phi \text{ (heating rate)}, \quad T = T_0 + \phi t \]
Rate of the process, $\alpha'$, is (manifestly ?) assumed to be proportional to the product of two separate functions: that is the rate constant $k(T)$, dependent solely on the temperature, $T$, and the mathematical portrayal of the reaction mechanism, $f(\alpha)$, reliant on the process variation of the degree of conversion, $\alpha$, only.

Kineticists believes in the exponential law of energy distribution, $k(T) = A \exp (-E/RT)$, derived by Arrhenius for the stochastic process of evaporation and approved by Boltzmann statistics the experimenters because they think it can be proved mathematically, and the mathematicians because they believe it has been established by observations.
\[ \frac{d\alpha}{dt} = f(\alpha) A \exp\left(\frac{-E}{RT}\right) \]

Commonly accepted law for \( k(T) \)

Yet?

inconvenient alternative solution via \( \frac{d^y\alpha}{dt^y} \)

Finding and fitting suitable analytical form called model

Traditionally constant

Functional \( E(\alpha) \)
**Traditional kinetics:** the Arrhenius exponential parameter $k(T)$ is introduced and the $f(\alpha)$ function is modeled on basis of simplified physical-geometrical assumptions (growth/change of reaction interface)

**Phenomenological kinetics:** the Arrhenius exponential parameter $k(T)$ is maintained but the $f(\alpha)$ function is replaced by a suitable fitting (polynomials, fractal-based equations, etc.)

**Modern non-parametric kinetics:** e.g., mutually independent functions $k(T)$ and $f(\alpha)$ assume arbitrary function, i.e., both the Arrhenius parameter and model function are not connected with a specific reaction mechanism showing accidental-like relationship.
Fractals - logistic function
\[ \alpha^m (1 - \alpha)^n \]

Model-free kinetics or kinetic-less modeling
\[ \frac{d\alpha}{dt} = f(\alpha) \cdot k(T) \]

Functional form of activation energy
\[ \ldots A \exp\left(-\frac{E(\alpha)}{RT}\right) \]

Why not single \( f(x,y) \) or a polynomial ??

Fractals - logistic function
\[ \alpha^m (1 - \alpha)^n \]

Yet unconventional fractional calculus
\[ \frac{d^n \alpha}{dt^n} = \ldots \]


**Temperature control:** standard - linear (heating rate $\phi$) alternatives (more convenient)

<table>
<thead>
<tr>
<th>Program</th>
<th>$f(T) = at^m$</th>
<th>$a:$</th>
<th>$m:$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Linear heating</td>
<td>$\phi$</td>
<td>$\phi$</td>
<td>0</td>
</tr>
<tr>
<td>Exponential</td>
<td>$at$</td>
<td>$a$</td>
<td>1</td>
</tr>
<tr>
<td>Hyperbolic</td>
<td>$bt^2$</td>
<td>$b$</td>
<td>2</td>
</tr>
<tr>
<td>Parabolic</td>
<td>$1/ct$</td>
<td>$1/c$</td>
<td>-1</td>
</tr>
</tbody>
</table>

**Temperature function:** $K(T) \cong A \exp(-E/RT)$

Mutual relation between $A$ and $E = KCE$ a pure mathematical consequence having no new physical content but complicating evaluations (kinetic compensation effect)
Simple reaction-order model

Physical-geometrical models

Phenomenological models

Fractal-like geometry

$(f(\alpha))$
Mechano-
measurements ~
10 μm (>10^-2 mm)
(external heat response)
Optical-
measurements ~ 600 nm (5.10^-4 mm)
Electron microscopy ~ 10 nm (10^-5 mm)
X-ray-
measurements ~ 0.5 nm (10^-7 mm)

Recently novel internal (molecular) heat
Homogeneous

\[ \frac{dc}{dt} - kf(c) \]

Simplest: \((1 - \alpha)^n\)

Heterogeneous

Definitied by Fractional Conversion \(\alpha\) (\(f(\alpha)\)-kinetic model function)

Complex: \((1 - \alpha) \{\log(1 - \alpha)\}^n\)

Space dimensions

(1) 1D
(2) 2D
(3) 3D

\(f(\alpha)\)
Kinetic models of a phase transition

Continual model:

\[ \alpha = 1 \] (initial)

Discontinual model:

\[ \alpha = 0 \] (final)
Variants of kinetic models of a phase transition

continual model:

Discontinual model:

(initial) \& (final)
Traditional discontinuous mathematical play
as a common subject of kinetic papers
or how to manipulate kinetic equation most easily

\[
d\alpha/dt = f(\alpha) A \exp(-E/RT)
\]

- Logaritmization
- Finding singularity conditions
- Maxima/minima of derivatives
- Integration \( g(\alpha) \)
- Manipulation with \( \pi(E/RT) \) function

unorthodox solution by fractal-like derivatives
\[- \log \left[ \frac{\alpha'}{f(\alpha)} \right] = \text{const.} - \frac{E}{R} \]

\[\left\{ \frac{\Delta \log \alpha'}{\Delta \log (1-\alpha)} \right\} \text{ vs. } \left\{ \frac{\Delta 1/T}{\Delta \log (1-\alpha)} \right\} \]

\[(\alpha = \text{const} \Rightarrow)\]

\[\frac{\Delta \log \alpha}{\Delta (1/T)} = \frac{E}{R} = \frac{\Delta \log A f(\alpha)}{\Delta \ln (1/T)}\]

Ozawa-Flynn \(\uparrow\) \(\left(\Leftarrow \alpha' = \text{const}\right)\)

\[\alpha'' = 0 = \alpha'\max \left\{ \frac{E/RT_{\max}}{A/\phi} \exp(-E/RT_{\max}) \frac{df(\alpha)}{d\alpha} \right\}\]

Kissinger \(\Rightarrow \ln \left( \frac{\phi}{T_{\max}} \right) = \frac{E}{R} \left( \frac{1}{T_{\max}} \right)\)
Integral methods $\Rightarrow$ lower discrimination

$$g(\alpha) = \int \alpha \, d\alpha / f(\alpha) = T_0 \int T \, k(T) \, dT / \phi$$

Integration process must be reversible, depends on the integral $T_0 \int T \, k(T)$

Approximation $\pi(x)$

$$\pi(x) = 1 \text{ in the limit } \cong k(T) \, T_0 \int T$$

Extra term $[1 + E/RT]$?

? Plotting of log $g(\alpha)$ vs either $T$, log $T$, $1/T$?

? Overlapping of model functions $g(\alpha)$
Often overlooked equilibrium background

\[ \lambda = \alpha \lambda_{\text{eq}} \]

Non-stoichiometric oxides

Unconventional !!
Effect of environment

Equilibrium partial pressure

\[ \pi(x) - \pi(x)_{eq} \neq > 1 \]

Decomposition near equilibrium temperature

Effect of environment
Nucleation followed by growth

\[ g(\alpha) = \int \frac{d\alpha}{f(\alpha)} \]

<table>
<thead>
<tr>
<th>Model:</th>
<th>Symbol:</th>
<th>function f(\alpha):</th>
<th>integral form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nucleation-growth</td>
<td>Am ( (1-\alpha)[- \ln (1-\alpha)]^{1-1/m} )</td>
<td>([- \ln (1-\alpha)]^{1/m})</td>
<td></td>
</tr>
<tr>
<td>(JMAYK eq.) ( m = 0.5, 1, 1.5, 2, 2.5, 3 ) and 4 ( (Johnson-Meal-Avrami-Yerofeev-Kolmogorov) )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phase boundary</td>
<td>Rn ( n(1-\alpha)^{1-1/n} )</td>
<td>([1 - (1-\alpha)1/n])</td>
<td></td>
</tr>
<tr>
<td>n-Dim.:</td>
<td>n = 1, 2 and 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(equivalent to the concept of reaction-order n)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Diffusion controlled

| 1-dim. diffusion | Di | \( 1/2\alpha \) |
| 2-dim. diffusion | D2 | \(- [1/\ln(1-\alpha)]\) \( \alpha + (1-\alpha) \ln (1-\alpha)\) |
| 3-dim. diffusion | D3 | \( (3/2)(1-\alpha)^{2/3} /[(1-\alpha)-1/3- 1] \) \( [1 - (1- \alpha)1/3]2\) |
| (Jander)          |    |                  |
| 3-dim. diffusion | D4 | \( (3/2)/[(1-\alpha)-1/3 – 1] \) \( 1 - 2\alpha/3 – (1-\alpha)2/3\) |
| (Ginstling-Brounshtein) |    |                  |
| 3-dim.counter diff. | \( (3/2)(1+\alpha)^{2/3}/[(1+\alpha)-1/3 + 1] \) \( [(1+\alpha)1/3 - 1]2\) |
| (Komatsu-Uemura, sometimes called ‘anti-Jander’ equation) |

Normal grain-growth

\( (1 - \alpha)n+1/(n ron) \) \( [ro/(1 - \alpha)]n - ron\) \( \) (Atkinson – long-range diffusion where ro is initial grain radius)

Unspecified - fractal approach (extended autocatalytic)

<table>
<thead>
<tr>
<th>fractal-dimension</th>
<th>SB</th>
<th>( (1 - \alpha)^n \alpha^m )</th>
<th>no analytical</th>
</tr>
</thead>
</table>

Johnson-Mehl-Avrami-Yerofeyev-Kolmogorov

Atkinson – just a grain growth

Modeling of reaction mechanism
Phase boundary diffusion, sintering

Classical modeling by Euclidian geometry

Model grouping in three classes

Model representatives are circumferences representing interfaces
Space misfits

Space filling

Regular objects

Interface curvature

Fractal geometry
Adding an accommodation function to the simple $(1 - \alpha)^n$

$$\frac{(1 - \alpha)^n}{(q) \alpha^m}$$

allowed pairs $n-m, n-p$

fertility-mortality

exchangeable
Other models, phase boundary and/or nucleation/growth
Impact of heat upon the sample inner make up

Changes in vibrational and positional structure

Thermal analysis determination of heat changes

and its sink

upon the sample inner make up
Changes in vibrational and positional structure
Isothermal and non-isothermal measurements: naturally involves thermal setups-gradients

Why are the curves/peak by DTA and DSC different?

Mutual comparison of the sensitivity of measurements

Can we recognize its consequences?!
\[ \Delta T_{DTA} = [\Delta K(T_W - T_R) - (C_P^S - C_P^R) \Phi - C_P^S(d\Delta T/dt) + \Delta_t H.d\xi/dt]/K_{DTA} \]
\[ \Delta T \quad K_{DTA} = \]
\[ + \Delta H_S \xi' \]
\[ - (C_{p_{oS}} - C_{p_R}) \phi \]
\[ - \Delta C_{p_S} (\phi + \Delta T/dt) \]
\[ - C_{p_{oS}} \Delta T/dt \]
\[ + \Delta K(T) \]

1 - as-received DTA
2 - corrected DTA peak
3 - real (s-shaped) background
4 - approximated DTA peak baseline
5 - recorded i.e. actual DTA trace
6 - baseline shift due to

measured quantity 
enthalpy evolved 
heat capacity change 
inertia 
 transient 
 experimental constant
Previous: M.J. Vold (125 citations) provided her equation 8 in above reference as

\[(\Delta H/C_s)(d\alpha/dt) = - (d\Delta T/dt) - A(\Delta T - \Delta_0 T)\]

where \(\Delta_0 T\) means a level of signal background, \(C_s\) is heat capacity of sample and \(A \approx K/C_s\). The equation (which is nearly equivalent to our equation) was obtained via a complicated derivation which is starting with a typing error “\(dH/dt = (dH/dt)(dT/dt)\)” what could be a reason why the equation was not very credible for a majority of thermoanalysts. The results of Vold was detailed by I. Proks [42] who combined them with results of others authors to derive the dependences of peak area and of position and height of extreme deviation (on the DTA curve) upon heating rate.

In 1957 the mentioned inertia term was used by H.J. Borchard and F. Daniels (824 citations) who applied DTA to study kinetics of homogeneous reactions in well stirred liquid samples showing:

\[dH = C_P d\Delta T + K\Delta T dt\]

from which our equation can be obtained by substituting \(dH = \Delta H d\alpha\) and then dividing their equation by \(dt\). The correction with respect to heat inertia is included also in their equation expressing the rate constant \(k\) of homogeneous reaction

\[k = (C_p(d\Delta T/dt) + K\Delta T)/(K(A-a) - C_p\Delta T)\]

(where \(A\) is total area of peak and \(a\) is a part of this area for time \(t = t_h\)).
Effect of heat inertia on kinetic evaluations

Evaluation of kinetics and mechanism by SQUEST

Phase transition of BaCO$_3$ at 810° C
\[ \Delta H \quad E \ [\text{cal}] \]
mechanism
613 118 A3
617 52 A3

Inertia rectifying evaluation program by ALANTA: Holba P, Nevřiva M, Šesták J. Analysis of DTA curve and related calculation of kinetic data using
Temperature of ultrafast changes in nano-scale and its determinability

$\Delta q \Delta T = ?\Delta?$

Where is the operate limit of uncertainty principle

$\Delta T/\Delta t = ?\Delta?$

Where is the operate limit of ever recordable temperature changes

$\Delta T = ?\Delta?$

Where is the limit of readable and reproducible temperature gradient

Yet further problems at the nano-scale physics:

Heat transfer on submicro- and nano-scales differs from that at macro scale due to:

Finite size of gas gaps (molecules, species); so called ballistic effect

Finite thickness of solid domains (photons, electrons) ⇒ ballistic effect

In narrow gaps heat flux limited by velocity and concentration of molecules

Destructing effects on phase interfaces (including destructive interference - phase interface does not have volume)

Thermal photon tunneling (evanescent waves)
Stationary versus dynamic heat capacity

Portrayal of the initial evolution of unstable and stable interfaces when imagining a planar section of a reacting sample interface (middle circle). During propagation, any such interface will become a subject to random (but spatially regular) disturbances caused by temperature fluctuations, variations of grain boundaries, curvature, insoluble subdivisions, concentration alternations, energy irregularities, etc.

Any unstable interface (upper row) is distinguished from a stable interface (lower row, traditionally assumed in all physical-geometrical modeling) by its sensible response to such disturbances which in an equilibrium approach does not occur.

Use of functional-like resulting data

Non-equilibrium processes – dendrites, sells, crystallites

Classical kinetics – traditional models from simplified geometry
Effect of supercooling and oversaturation:

Macro-scale dendrite formation

Organized Bernard cells illustrating ever existing effect of contrary fluxes (due to the opposite outcome of heat and gravitation)

Micro-scale (casing of microorganism):

Real growth of:
Sells
Crystallites
Dendrites
Smog, snow, etc
Theory of chaos: boundary between order and disorder

Significance of limits and self-similarity

General validity of power laws

Integral (Euclidean) and non-integral (fractal) dimensionality

Deterministic chaos, periodic points and logistic functions

Competition laws: controversial between fertility ($x$) and mortality ($1-x$)

Bifurcations and separation tendency
Necessarily use of fractal geometry

Irregular aggregations instead of regular

Generality of power law $x \sim y^n$

Impact of power law

Dense

Irregular aggregations instead of regular
Thermophysics of chemical reactions

Morphological & fractal self-similarity

Titanium surface after an alkali treatment

hydroxyapatite growth pattern

snow flags

melt solidification
Self-similarity and order of pattern growth

ΔT

Gradient controlled

2D-growth of high $T_c$ YBCO superconduc.: spacing between spiral is inversely proportional to $\Delta T$ and the growth rate to $(\Delta T)^2$ (Hilling, Turnbull, J.Chem.Phys. 1958)

crystal growth of ammonite (left)
life-grown structures of shells (right)
Repetitive structures

co-centric patterns of some natural formations and Liesegang’s rings of silver chromate crystallites

directionally solidified dielectric eutectic of PbCl2-AgCl

ornamentally casing work of micro-organisms based on calcite structures

Quantum impact: $K_m \lambda u = h$
reactants $\rightarrow$ A
products $\downarrow$ $\uparrow$
reactants $\rightarrow$ B + X $\rightarrow$ Z + Y
products $\leftarrow$ P $\leftarrow$ 3X $\Leftrightarrow$ 2X + Y

Self-catalysed reactions

Irregularly mixed powders
Processes at the eutectics and peritectics

Lamella periodicity

\[ \text{dA} \rightarrow \text{diffusion} \rightarrow \text{dA} \]
\[ \downarrow \text{react} \quad \downarrow \downarrow \quad \downarrow \text{react} \]
\[ \text{dB} \rightarrow \text{diffusion} \rightarrow \text{dB} \]

\text{reaction} \downarrow \text{interface}

microgravity terrestrial growth coarsening
Kinetics of periodic reactions

Classical diffusion

Fick law $D = 1, 2, 3$

Hausdorff’s dimension & measure, $D_n = 2$

Brownian motion

Quantum criterion

$M \nu \lambda = h$
Conferences:

„Frontiers of quantum and mesoscopic thermodynamics“ Praha, July 2004

„New frontiers of thermal studies of materials“ Tsukuba (Japan), November 2004
Liesegang rings and BZ spiral

Maupertuis
(1768)
“Principle of least action”
Periodical shapes in the nature

Fermat’s principle (1630)
of shortest reaction time
New book on the market
by Elsevier, Amsterdam
December 2005

Thank you for your very patient attention

This study was supported by grant No A100100639 of the Grant Agency of Czech Academy of Sciences and project MSMT 4977751303 by the West Bohemian University.
Hopefully to see you again in near future and welcome sometimes to ‘golden’ Prague.

Fractal structures are real.