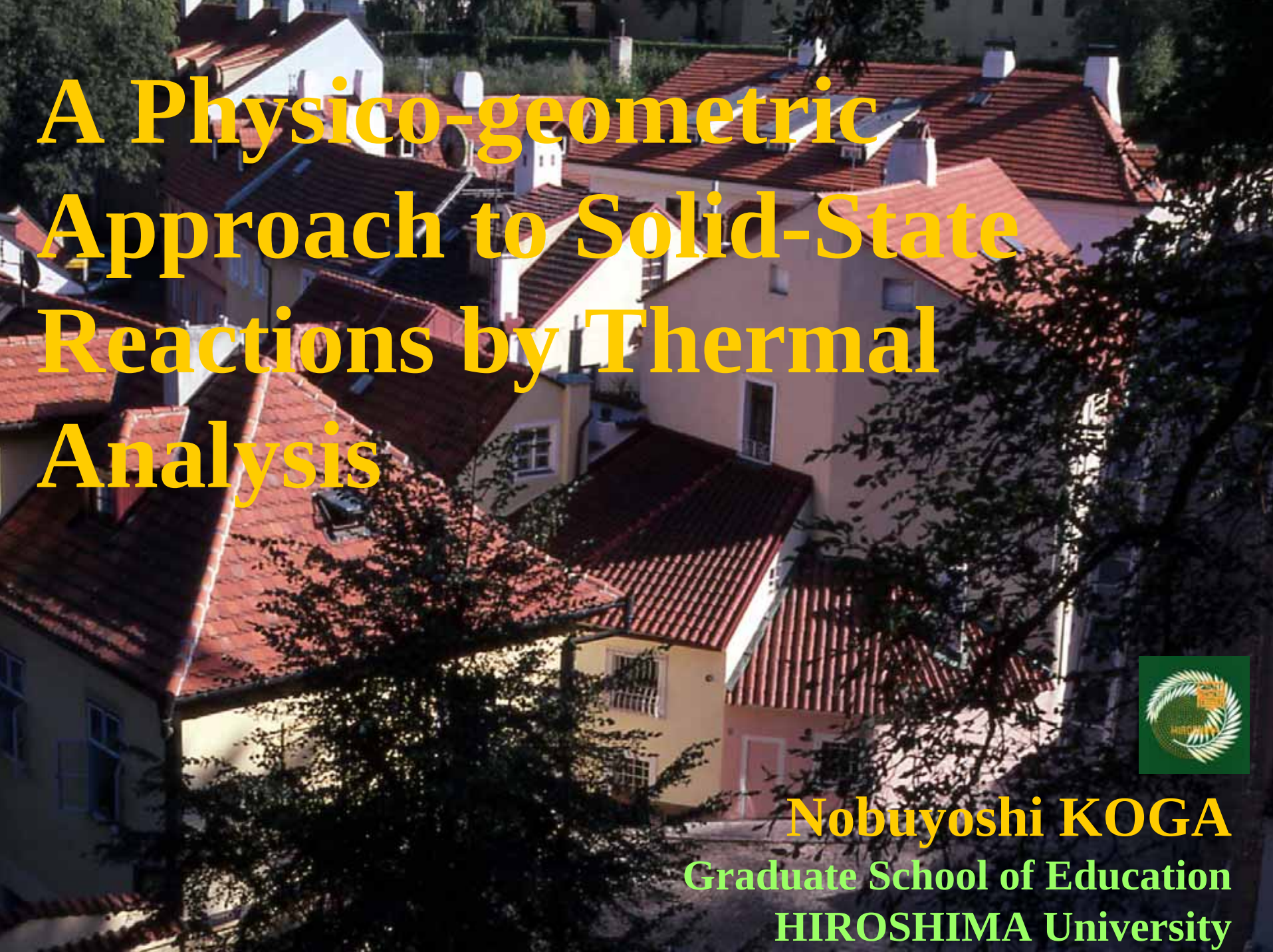
A Physico-geometric Approach to Solid-State Reactions by Thermal Analysis



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Theme:

How to characterize the overall kinetics of the solid-state reactions from physico-geometric points of view?

Contents:

(1) Physico-Geometry of Solid-State Reactions
(2) Kinetic Model Functions
(3) Kinetic Equations
(4) Application of Thermoanalytical Method
(5) Sample Controlled Thermal Analysis
(6) Concluding Remarks

ex. Thermal Decomposition of Solids

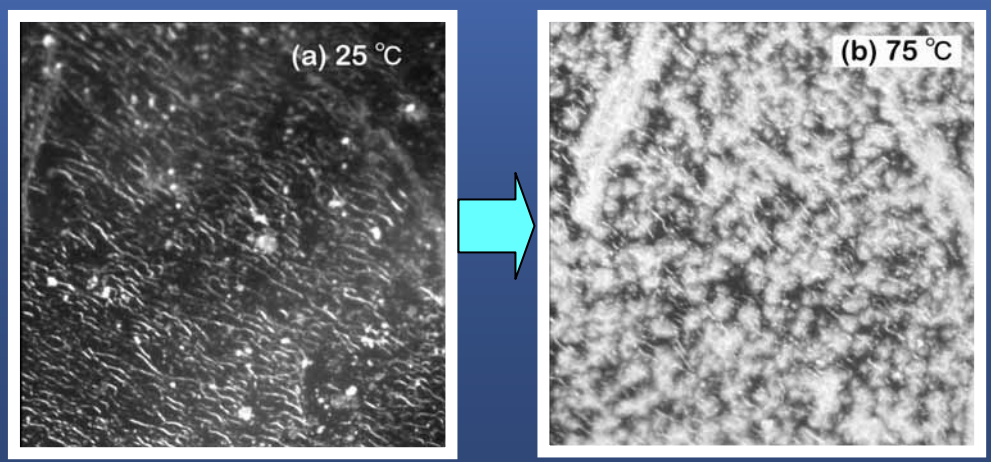
Reactant Surface ⇐ one of the most reactive sites

⇓

Reaction initiates by nucleation and growth

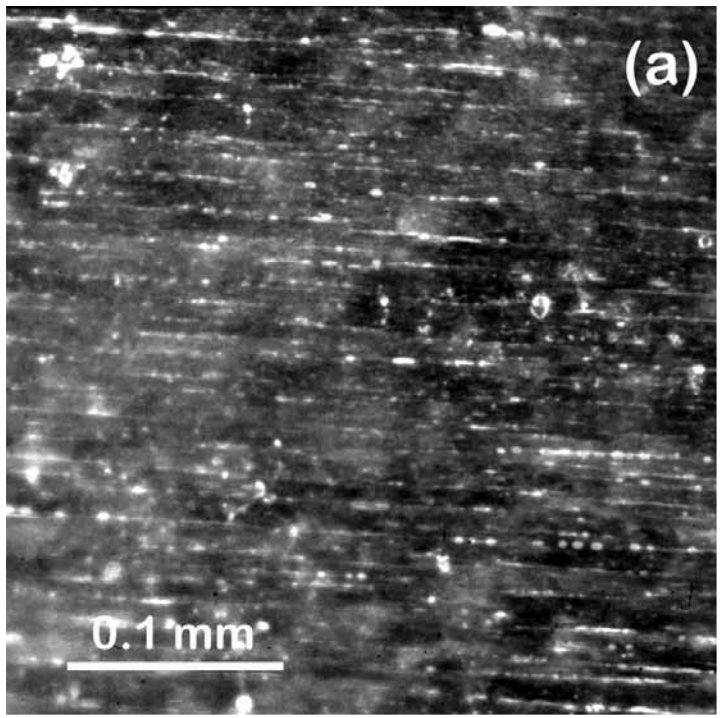
⇓

- Surface defects and dislocations
- Crystallographic direction
- Reaction atmosphere
- Others



Nonisothermal dehydration of α-$NiSO_4 \cdot 6H_2O$ to tetrahydrates under flowing N_2.

☐ Relation to Crystallographic Direction



Isothermal dehydration of zinc acetate dihydrate to anhydride under flowing N_2.

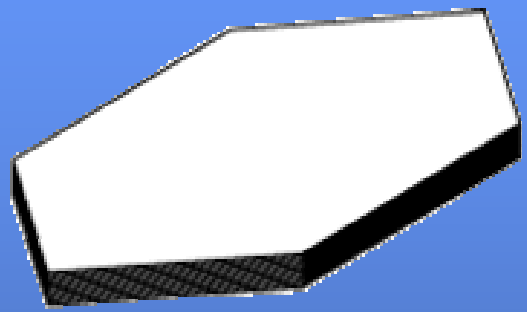


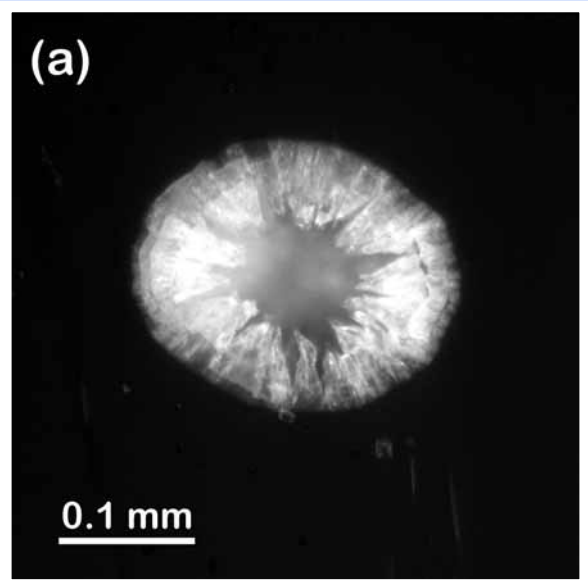
plate-like single crystals with stacking layer structure

Edge surface

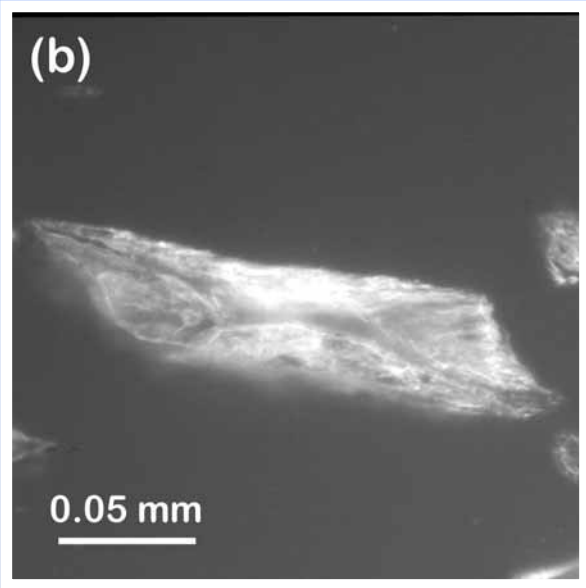
⇐ The most reactive sites

Product nuclei appear parallel to the most developed surface (010)

☐Influence of Reaction Atmosphere



Under flowing N_2



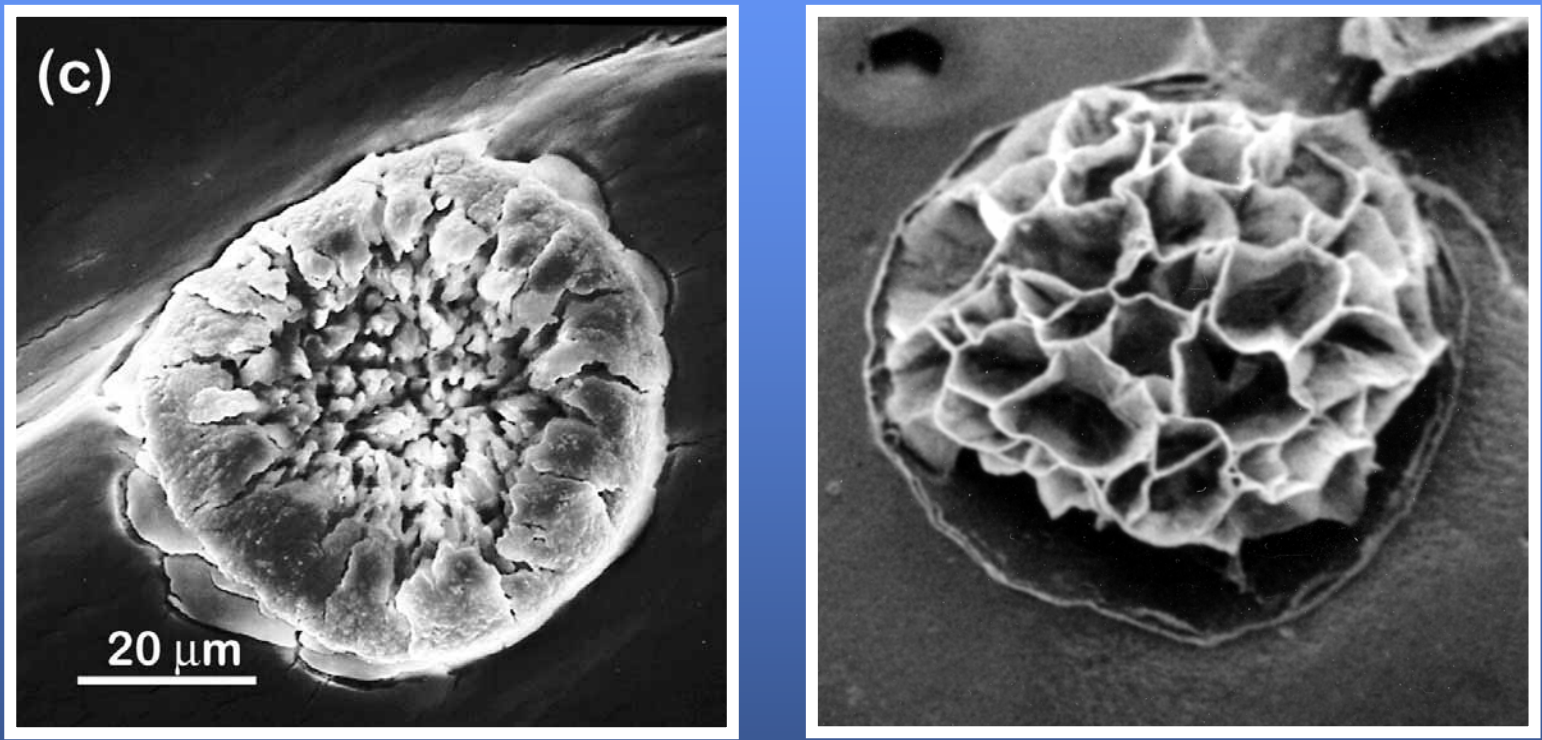
At a reduced pressure of 1.5 hPa

⇨ Formation of trihyrate nuclei

⇨ Formation of monohydrate nuclei

Isothermal dehydration of copper(II) sulfate pentahydrate

Structure of Product Nuclei



Isothermal dehydration of copper(II) sulfate pentahydrate to trihydrate.

Classification of Product Nuclei

Classification	Characteristics	Example
Fluid-flux	Retention of a volatile product at interface condensed as liquid	Dehydration of alum $KBr+Cl_2 \rightarrow KCl+BrCl$
Fusion	Product melting facilitates reaction	Decomposition of ammonium dichromate and copper(II) malonate
Functional	Strain and/or heterogeneous catalytic breakdown of intermediate at reaction interface	Decomposition of copper(II) formate, nickel formate, nickel aquarate and silver malonate
Flux-filigree	Two-zone structure of reaction interface	Dehydration of $Li_2SO_4 \cdot H_2O$

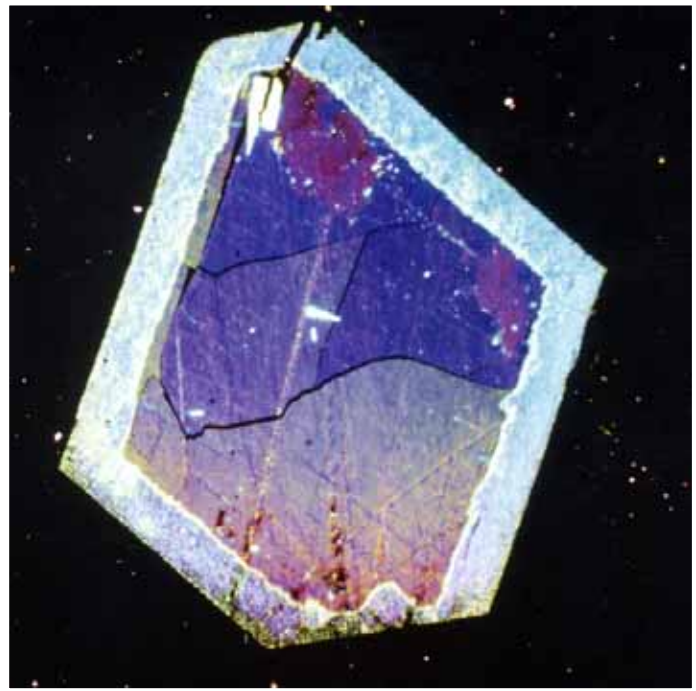
Reaction Interface (1)

Reaction Interface ⇐ A zone of locally enhanced reactivity located at reactant/product contact

⇓

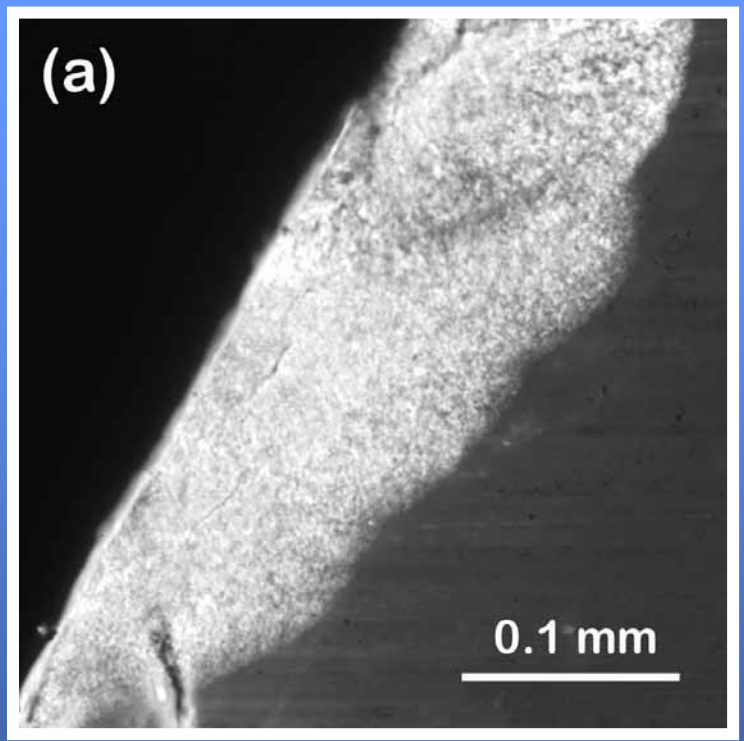
Reaction proceeds by advancement of reaction interface towards the center of reactant crystal

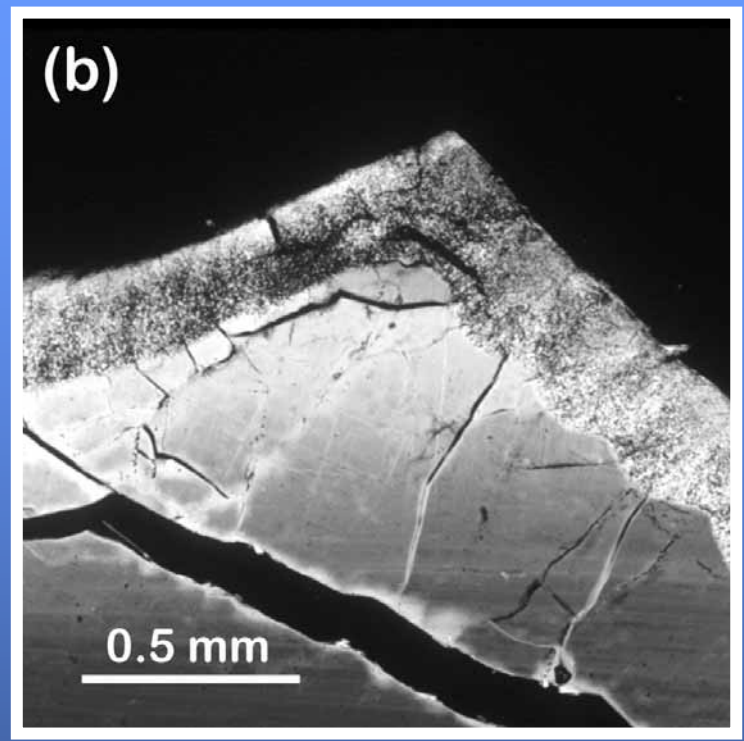
⇒
- Crystallographic direction
- Shape of reaction front
- Structure of reaction interface



Isothermal dehydration of copper(II) acetate monohydrate

Example (1)



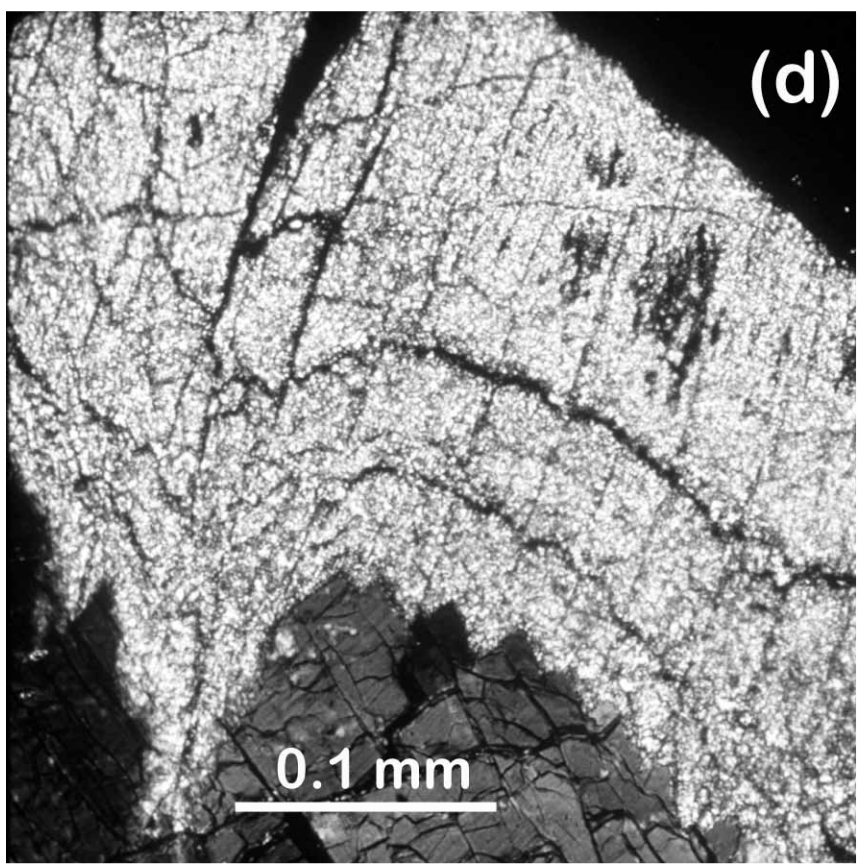


Surface nuclei ⇨ Growing hemispherically ⇨ Wavy front

overlap

Isothermal dehydration of lithium sulfate monohydrate to anhydride

Example (2)



Reaction front

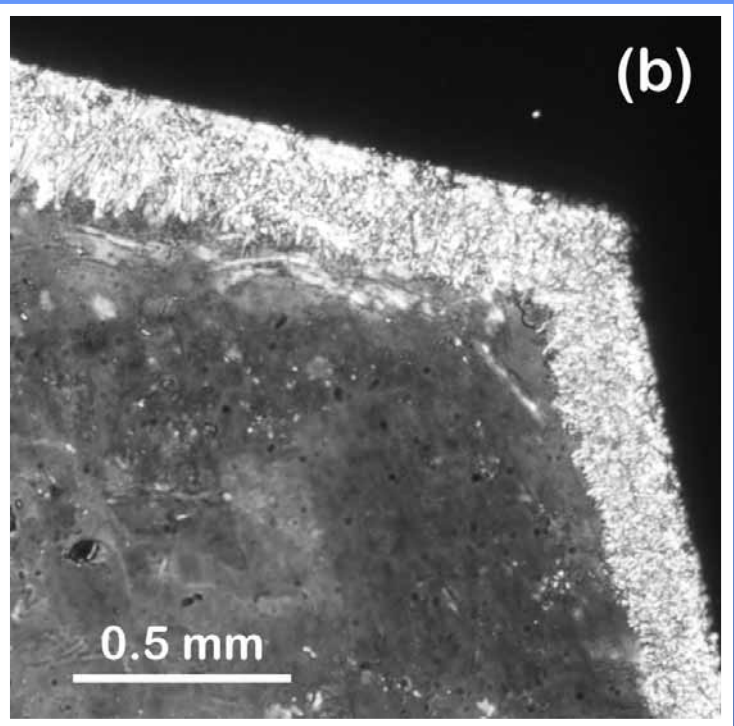
⇨ A saw-like shape

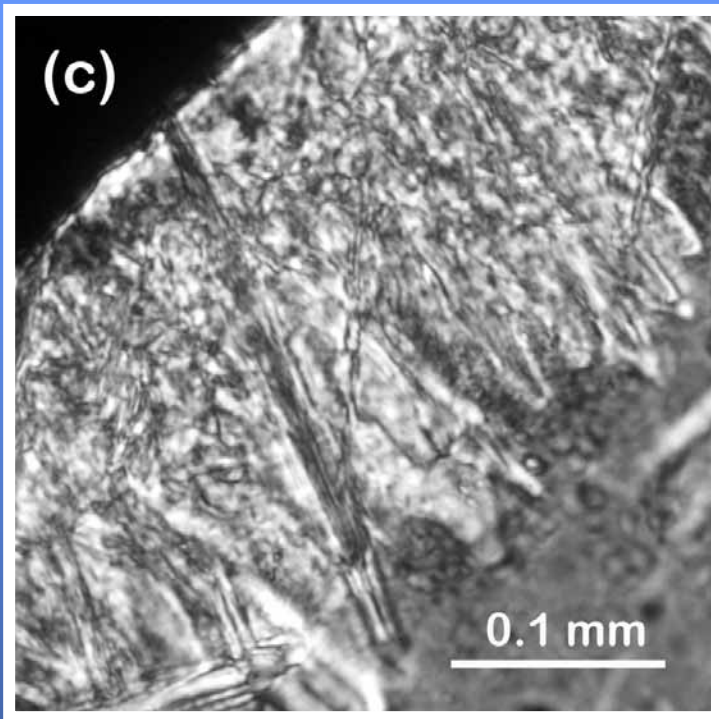
Product layer

⇨ A repeated stacking of dense and coarse aggregates of the product crystallites

Isothermal dehydration of copper(II) sulfate pentahydrate to trihydrate

Example (3)





Surface nucleation at edge surface of plate-like crystal

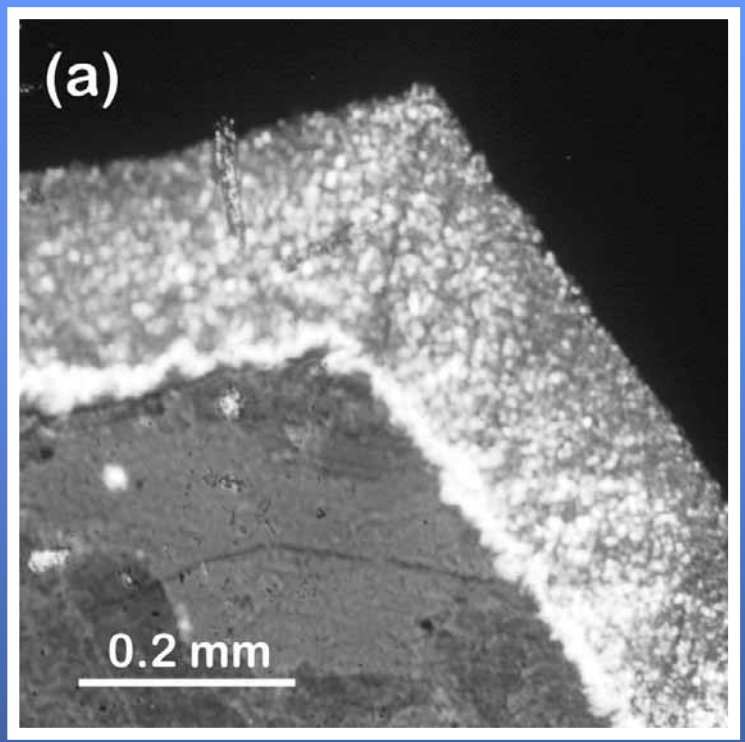
Reaction front

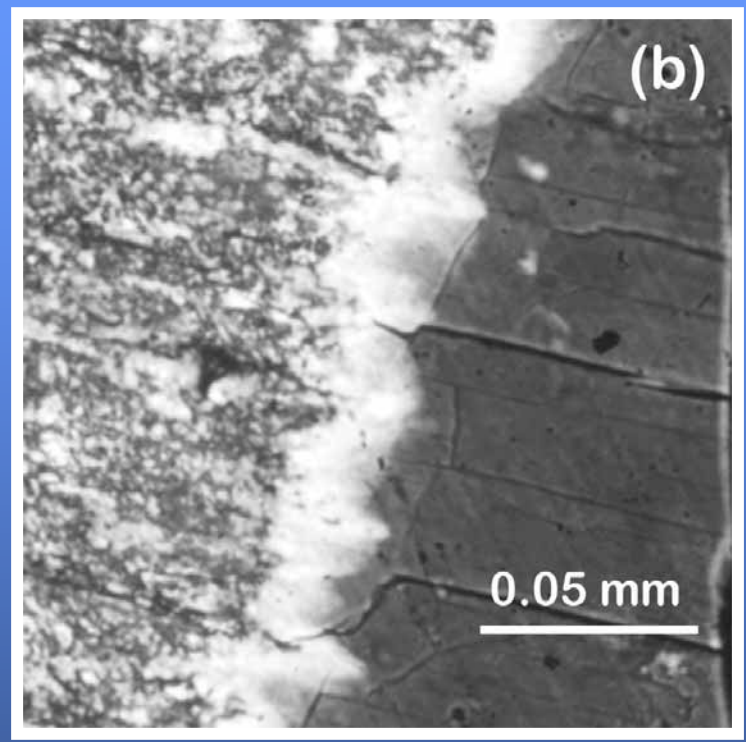
2D-shrinkage

- Needle-like product crystallites
- Penetration to reactant crystal

Isothermal dehydration of zinc acetate dihydrate

Example (4)

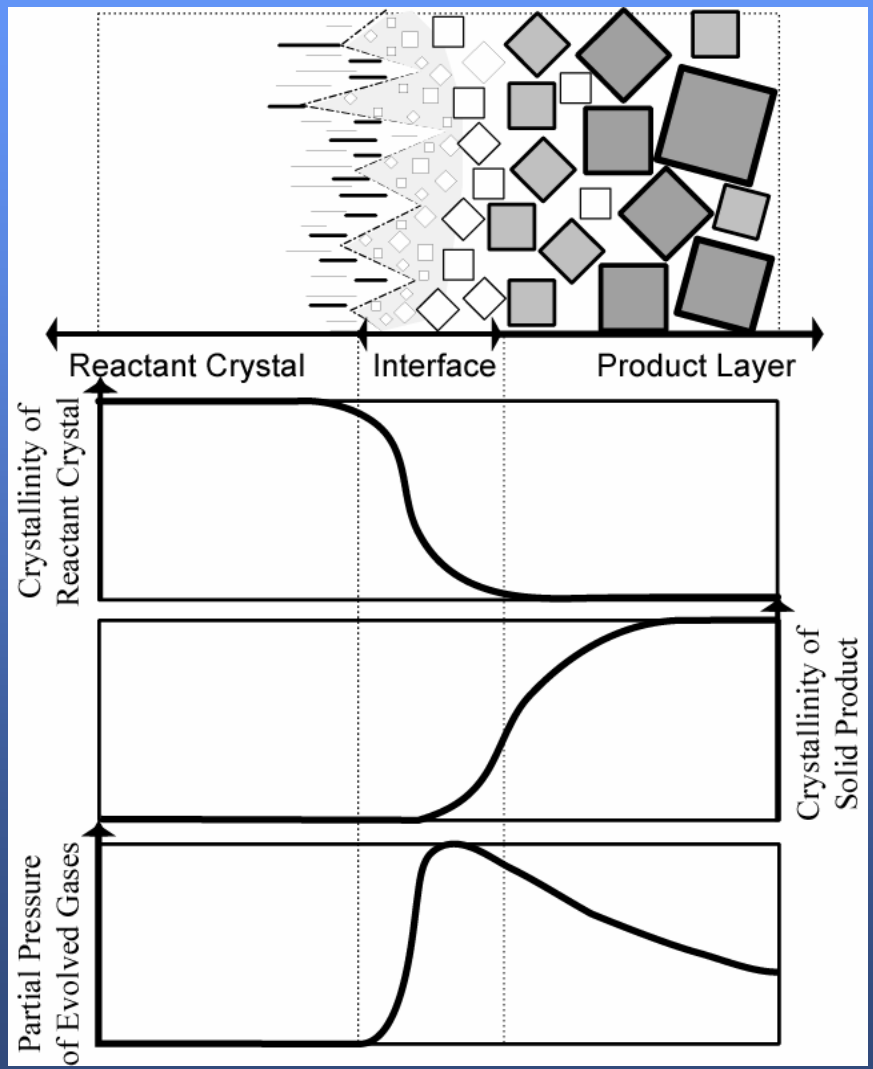




Reaction Interface ⇐ An optically different layer of 20~50mm thickness

Isothermal dehydration of copper(II) acetate monohydrate

A Model of Reaction Interface



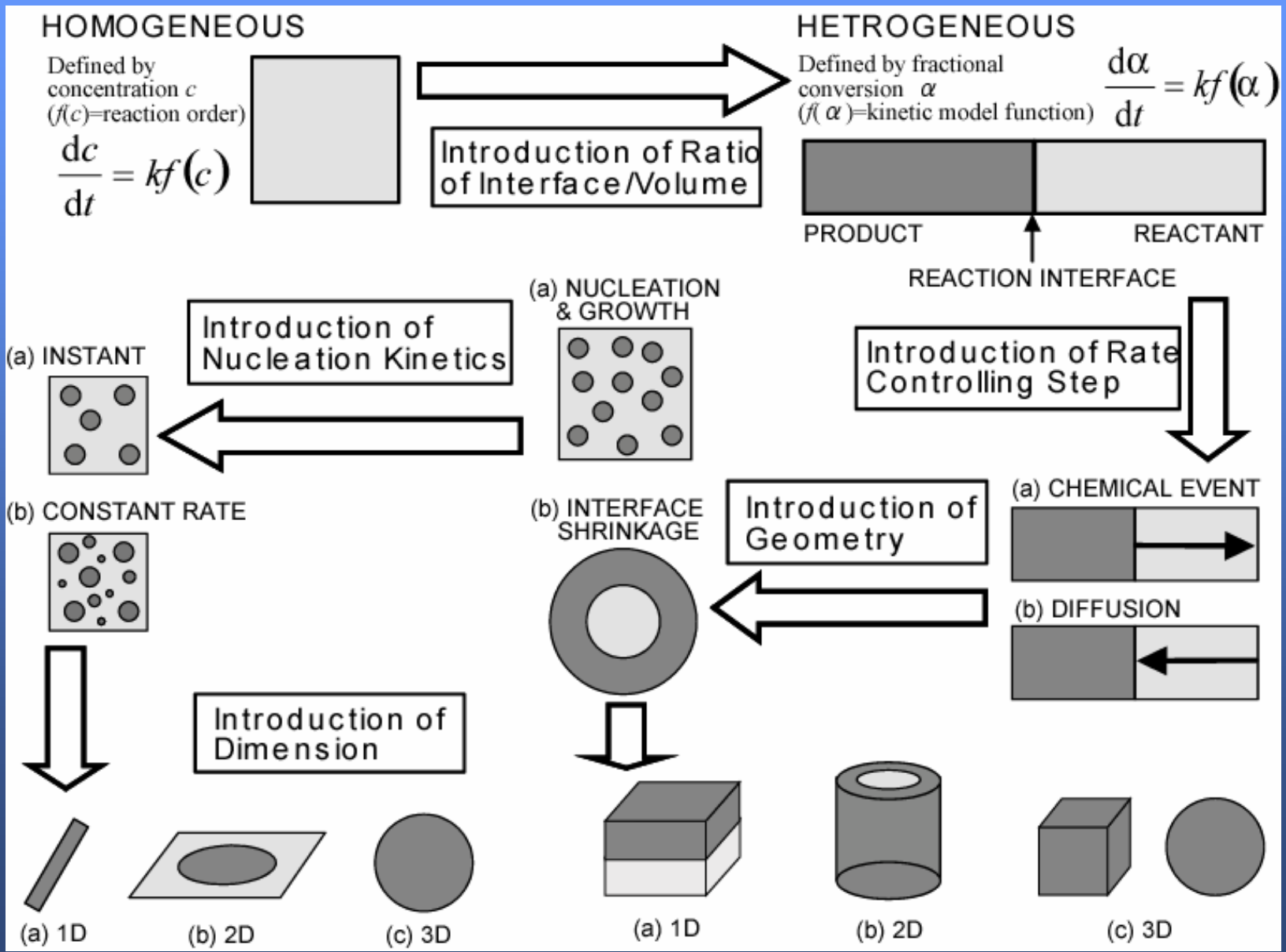
What is taking place?

ex. Thermal dehydration

- Water mobility within the crystalline reactant.
- Diffusive migration of water to crystal edge or interface.
- Water volatilization at the crystal edge of interface.
- Chemical reaction, if any.
- Recrystallization of solid reactant to product structure.
- Water vapor adsorption/ desorption on product solid.
- Intranuclear diffusive escape of water and loss beyond crystal.

A hypothetical transfer from homogeneous to heterogeneous model

Kinetic Model Function(1)



Kinetic Model Function(2)

Typical kinetic model functions for solid-state reaction

Model	Symbol	$f(\alpha)=\frac{1}{k}\frac{d\alpha}{dt}$	$g(\alpha)=\int_0^\alpha \frac{d\alpha}{f(\alpha)}=kt$
Nucleation & Growth	A_m ($0.5\le m\le 4$)	$m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m}$	$[-\ln(1-\alpha)]^{1/m}$
Phase Boundary Controlled	R_n ($1\le n\le 3$)	$n(1-\alpha)^{1-1/n}$	$1-(1-\alpha)^{1/n}$
Diffusion Controlled	D_1 (one D)	$\frac{1}{2\alpha}$	α^2
	D_2 (two D)	$-\frac{1}{\ln(1-\alpha)}$	$\alpha+(1-\alpha)\ln(1-\alpha)$
	D_3 (three D)	$\frac{3(1-\alpha)^{2/3}}{2\left[1-(1-\alpha)^{1/3}\right]}$	$\left[1-(1-\alpha)^{1/3}\right]^2$
	D_4 (three D)	$\frac{3}{2\left[(1-\alpha)^{-1/3}-1\right]}$	$1-\frac{2\alpha}{3}-(1-\alpha)^{2/3}$

General Kinetic Equation

- Physico-geometric Kinetic Model Function
- Temperature Dependence of rate constant
- Other functional dependence of reaction rate

$$\frac{d\alpha}{dt} = kf(\alpha)$$

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

$$\frac{d\alpha}{dt} \propto a(\alpha, T, P, ...)$$

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right) f(\alpha) a(\alpha, T, P, ...)$$

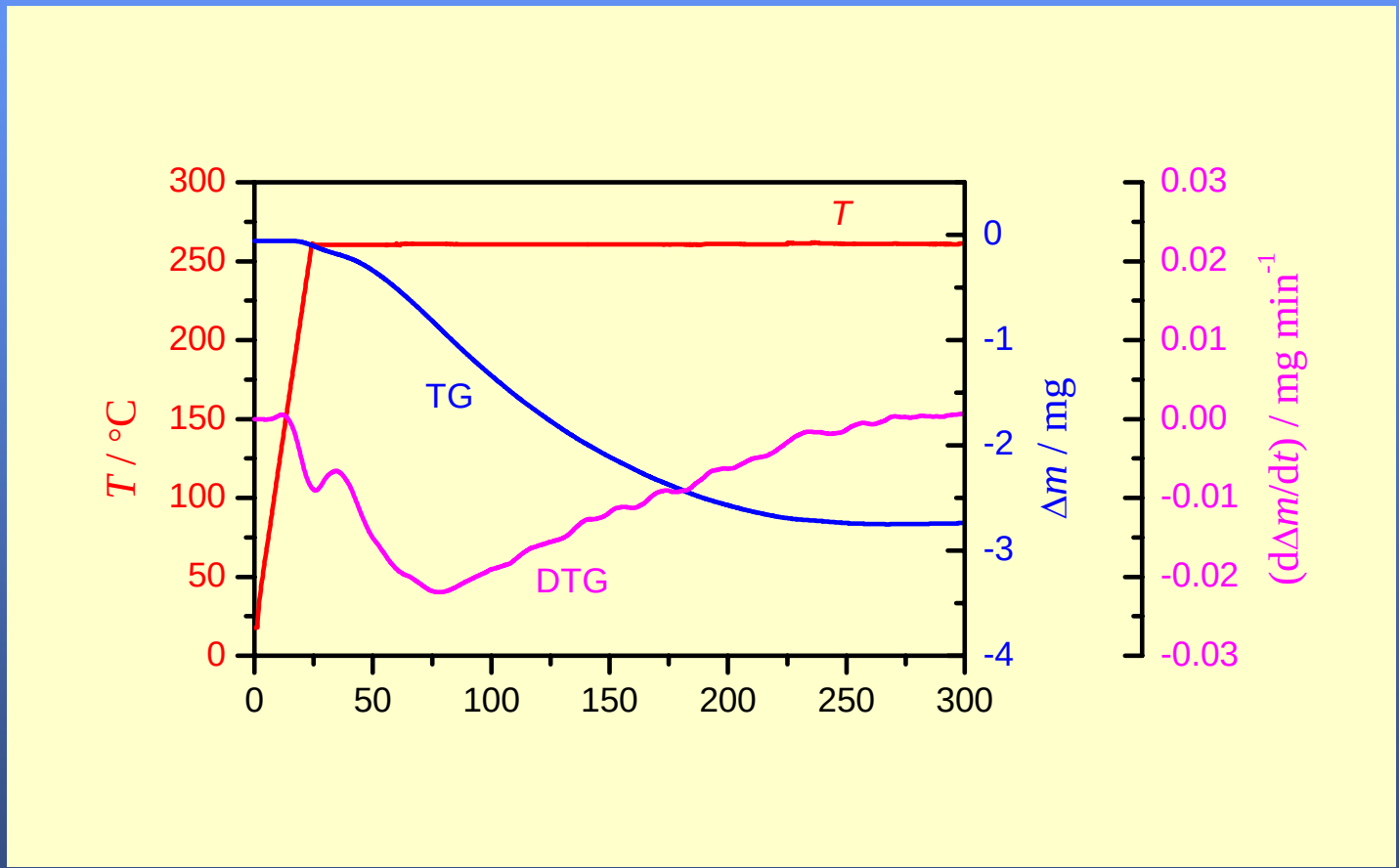
Idealized Kinetic Equation

$$a(\alpha, T, P, ...) = 1$$

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

Technique	Measuring Property	Kinetic Rate Data
DTA	Temperature difference	(T_p, α_p)
TG	Mass change	($d\alpha/dt$, α, T, t)
DSC	Heat flow rate	($d\alpha/dt$, α, T, t)
EGA	Evolved gas	($d\alpha/dt$, α, T, t)

(1) Measurement of Isothermal mass-loss data



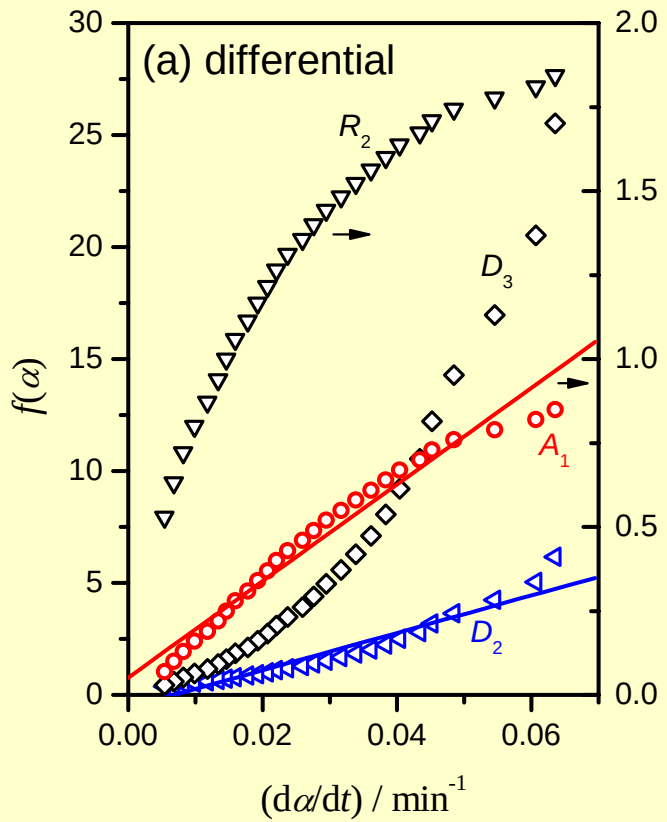
(2) Determination of rate constant *k*

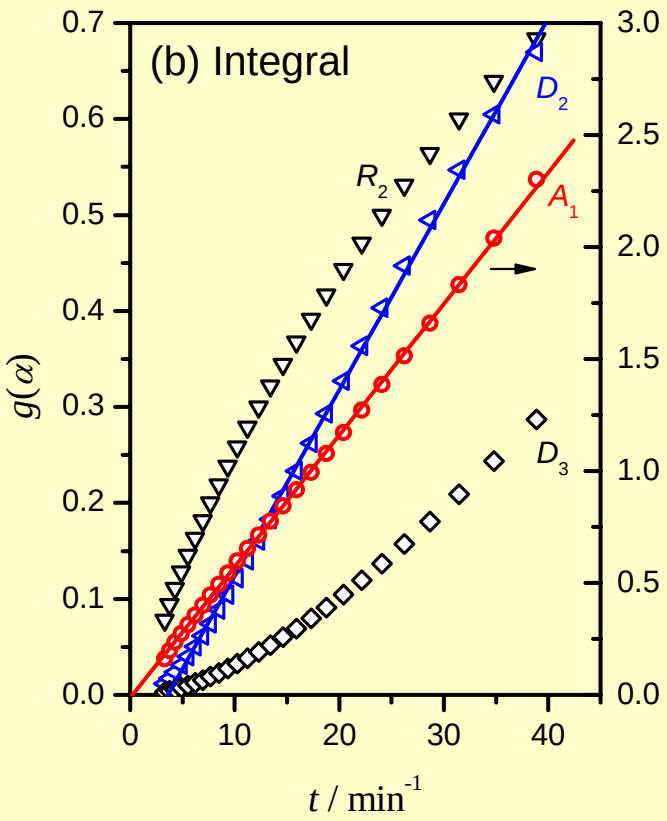
(a) Differential

$$\frac{d\alpha}{dt} = kf(\alpha)$$

(b) Integral

$$g(\alpha) = kt$$

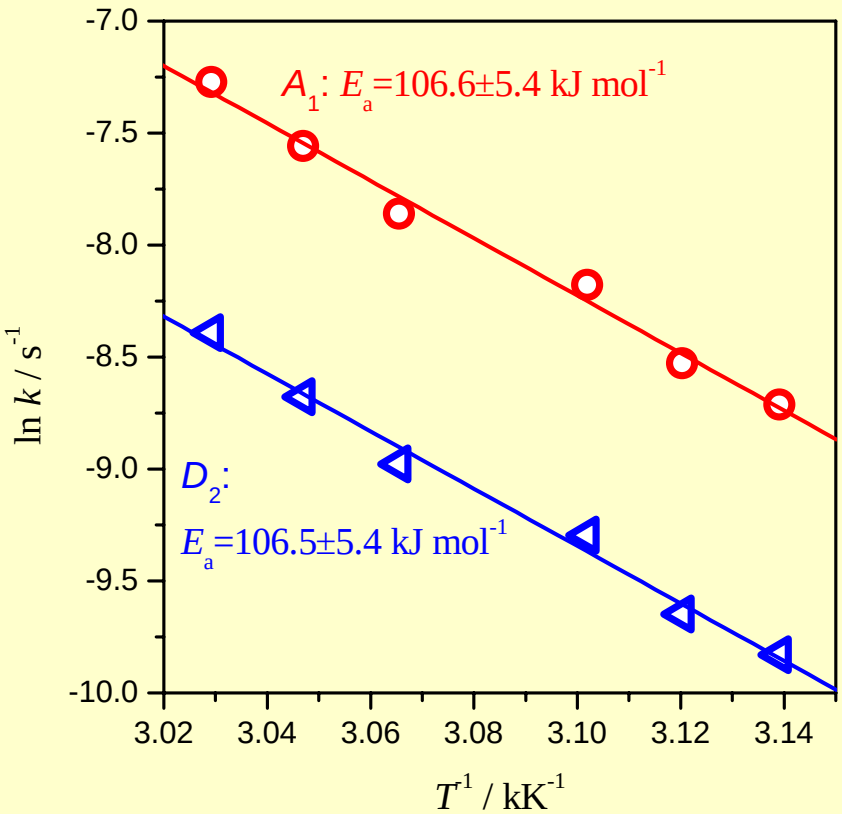




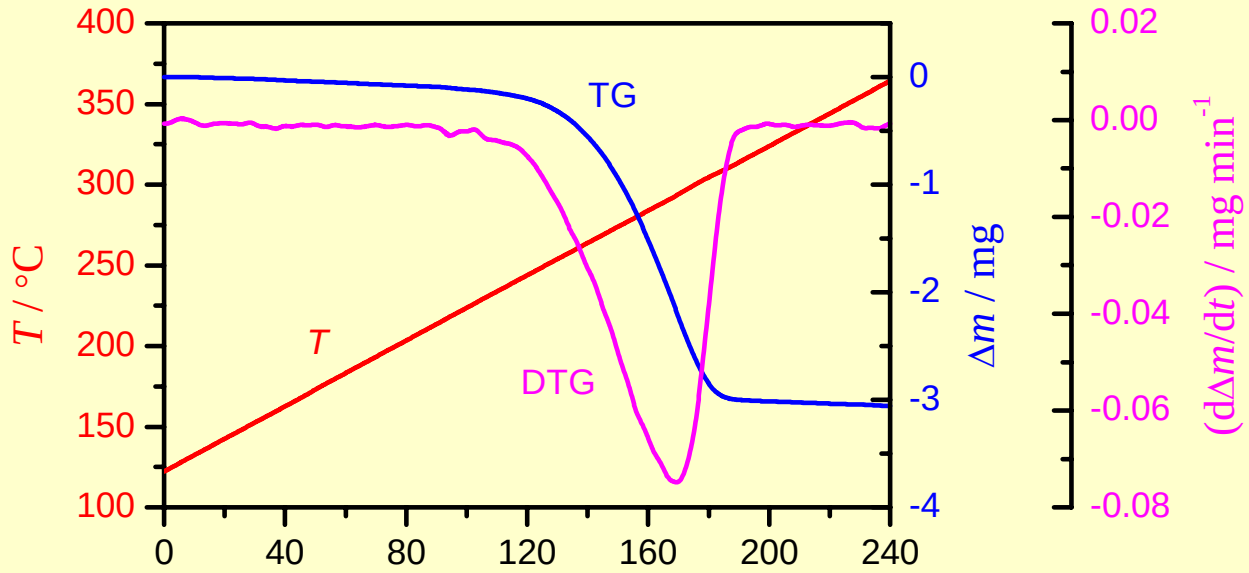
(3) Determination of *E* & *A*

Arrhenius plot

$$\ln k = \ln A - \frac{E}{RT}$$



(1) Measurement of Nonisothermal rate data



From single TA run

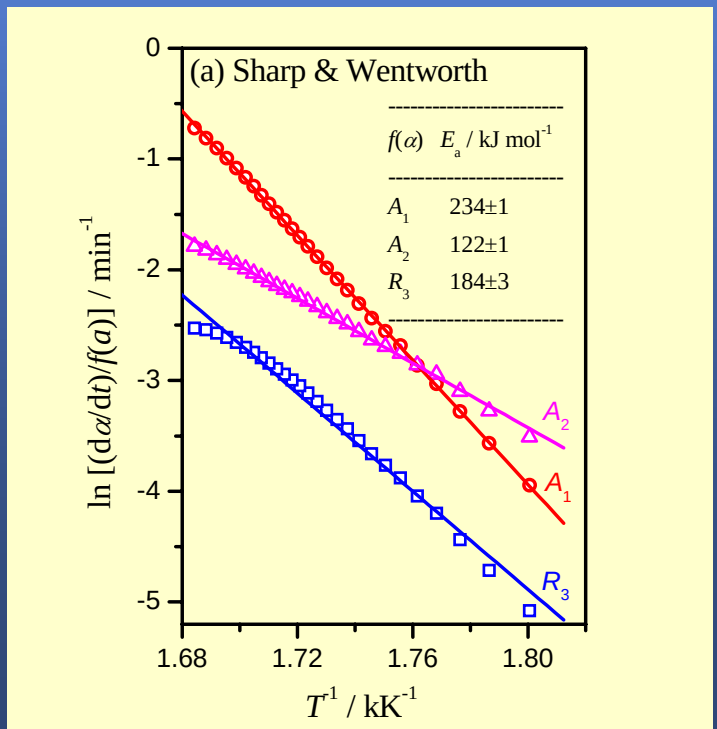
Nonisothermal Analysis(2)

At ϕ=const. $\Rightarrow$ $\begin{cases} T = T_0 + \phi t \\ \dfrac{d\alpha}{dt} = \dfrac{d\alpha}{dT}\phi \end{cases}$

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

1) Differential

$$\ln\left[\left(\frac{d\alpha}{dT}\right)\frac{\phi}{f(\alpha)}\right] = \ln A - \frac{E}{RT}$$



2) Integral

$$g(\alpha) = \int_0^{\alpha}\frac{d\alpha}{f(\alpha)} = \frac{A}{\phi}\int_{T_0}^{T}\exp\left(-\frac{E}{RT}\right)dT = \frac{AE}{\phi R}p(x)$$

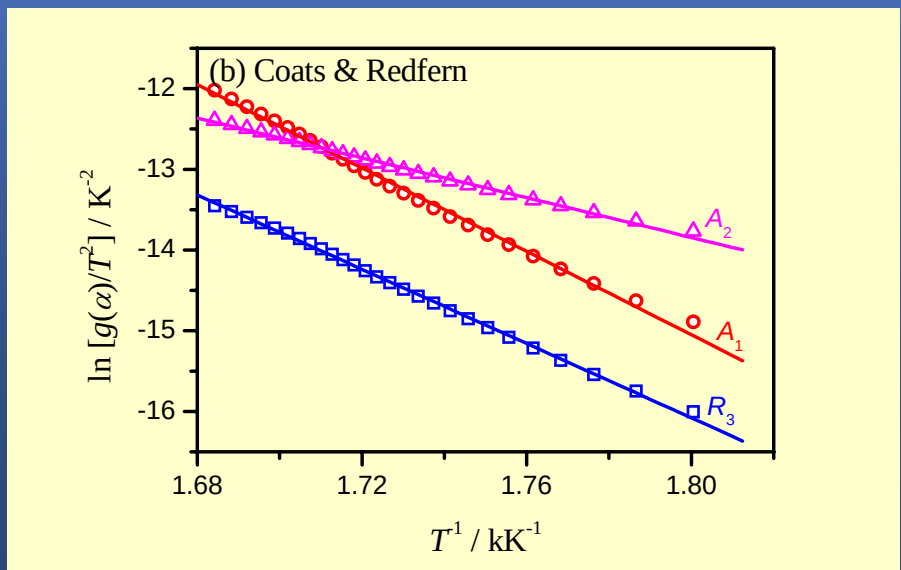
with $x = \dfrac{E}{RT}$

$$p(x) = \frac{\exp(-x)}{x} - \int_x^{\infty}\frac{\exp(-x)}{x} \cong \frac{\exp(-x)}{x}\pi(x)$$

For example

Coats & Redfern method $\pi(x) = \dfrac{x - 2/x}{x}$

$$\ln\frac{g(\alpha)}{T^2} = \left[\ln\frac{AE}{\phi R}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT}$$



From a series of TA runs

Nonisothermal Analysis(3)

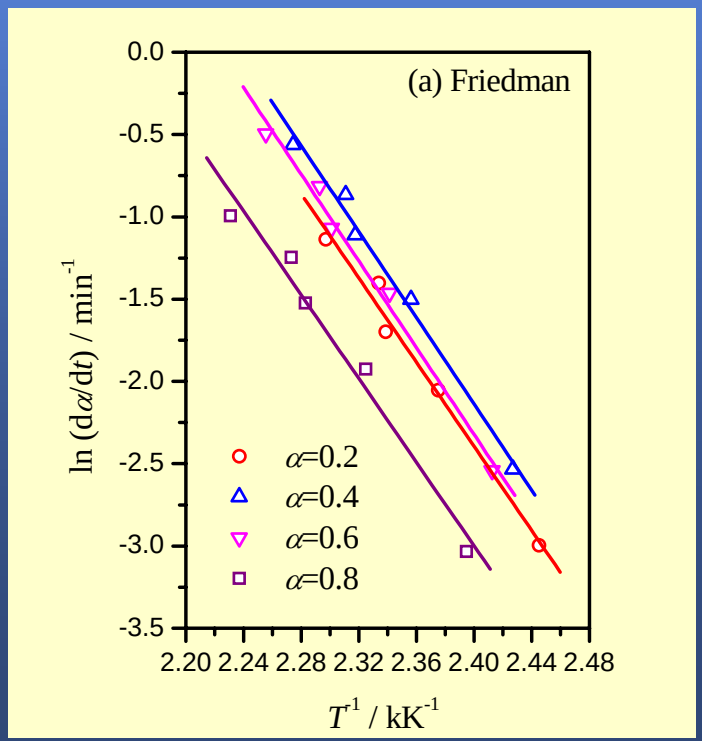
Isoconversional method

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

1) Differential

⇨ Friedman method

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln[Af(\alpha)] - \frac{E}{RT}$$



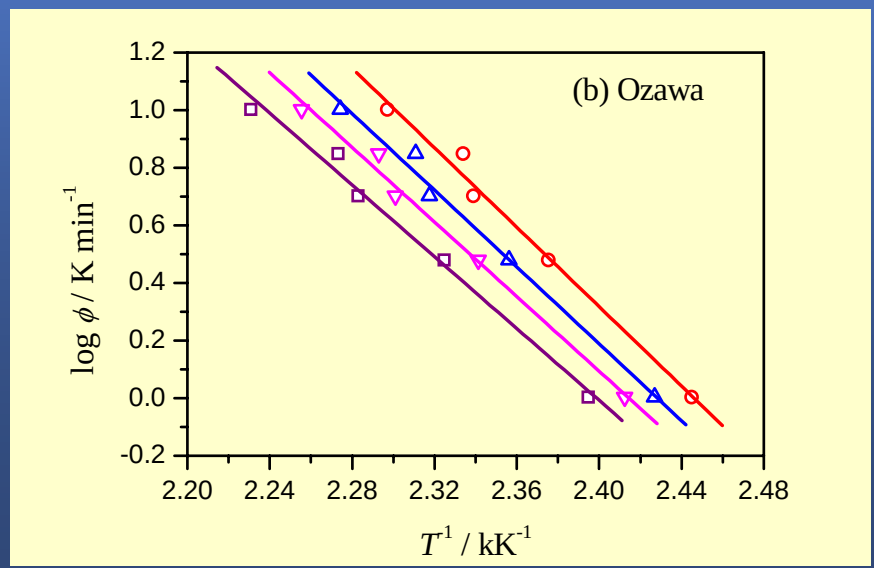
2) Integral

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\phi}\int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right) dT = \frac{AE}{\phi R} p(x)$$

with $x = \frac{E}{RT}$

⇨ Ozawa method $\log p(x) = -2.315 - 0.4567\frac{E}{RT}$

$$\log\phi = \log\frac{AE}{g(\alpha)R} - 2.315 - 0.4567\frac{E}{RT}$$



Nonisothermal Analysis(4)

From a series of TA runs

Peak method ⇨ Kissinger method

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

First derivative with respect to *t*

$$\frac{d^2\alpha}{dt^2} = A\exp\left(-\frac{E}{RT}\right) f(\alpha)\left[\frac{df(\alpha)}{d\alpha} A\exp\left(-\frac{E}{RT}\right) + \frac{\phi E}{RT^2}\right]$$

○ First order equation

$f'(\alpha)=-1$

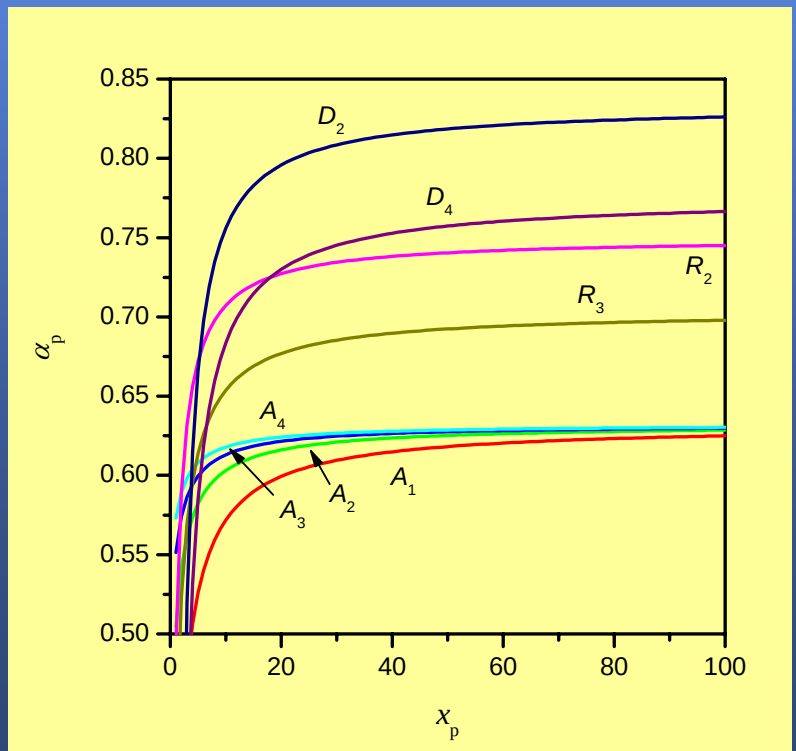
△ For other kinetic models

At peak maximum

$$\left(\frac{d^2\alpha}{dt^2}\right)_p = 0$$

$$\ln\frac{\phi}{T_p^2} = \ln\left[\frac{f'(\alpha_p)AR}{E}\right] - \frac{E}{RT_p}$$

with $f'(\alpha) = \dfrac{df(\alpha)}{d\alpha}$



Kinetic Master Plot

Nonisothermal Analysis(5)

Isothermal

1) Differential

$$\frac{d\alpha}{dt} = kf(\alpha) \Rightarrow \frac{f(\alpha)}{f(0.5)} = \frac{(d\alpha/dt)}{(d\alpha/dt)_{\alpha=0.5}}$$

2) Integral

$$g(\alpha) = kt \Rightarrow \frac{g(\alpha)}{g(0.5)} = \frac{t}{t_{\alpha=0.5}}$$

Nonisothermal

Introduction of generalized time θ

$$\theta = \int_0^t \exp\left(-\frac{E_a}{RT}\right)dt$$

1) Differential

$$\frac{d\alpha}{d\theta} = Af(\alpha) \Rightarrow \frac{f(\alpha)}{f(0.5)} = \frac{(d\alpha/d\theta)}{(d\alpha/d\theta)_{\alpha=0.5}}$$

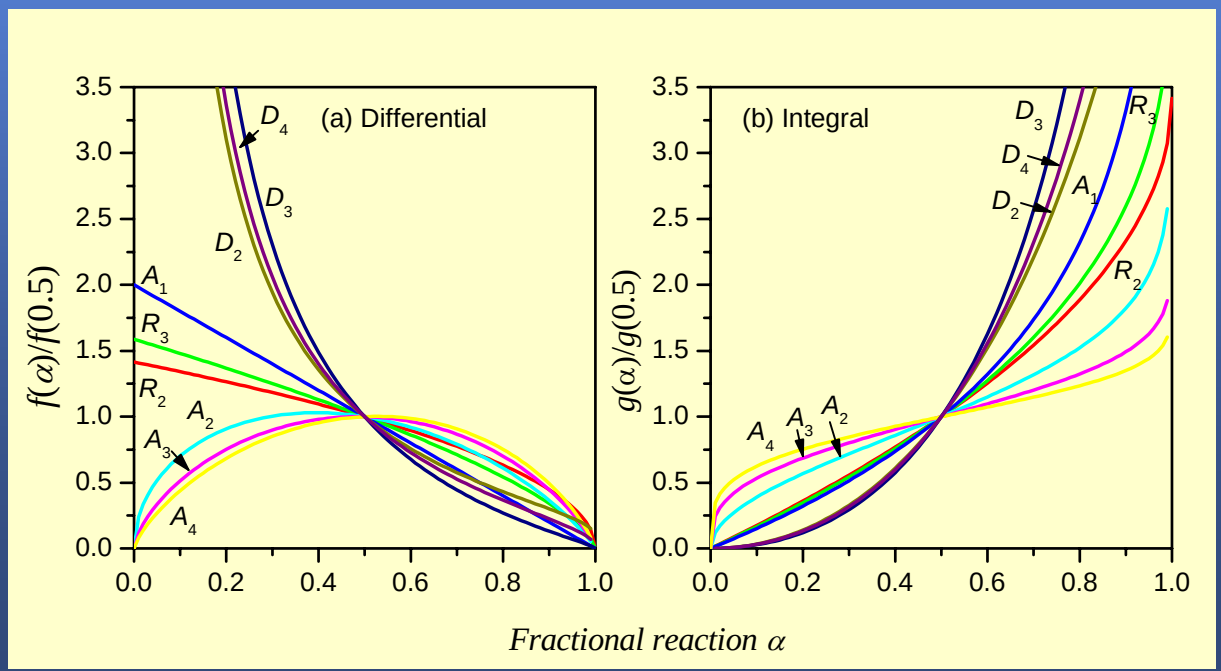
$$\frac{d\alpha}{d\theta} = \frac{d\alpha}{dt}\exp\left(\frac{E_a}{RT}\right)$$

2) Integral

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A\int_0^\theta d\theta = A\theta$$

$$\frac{g(\alpha)}{g(0.5)} = \frac{\theta}{\theta_{\alpha=0.5}}$$

$$\theta = \frac{E_a}{\beta R}p(x)$$



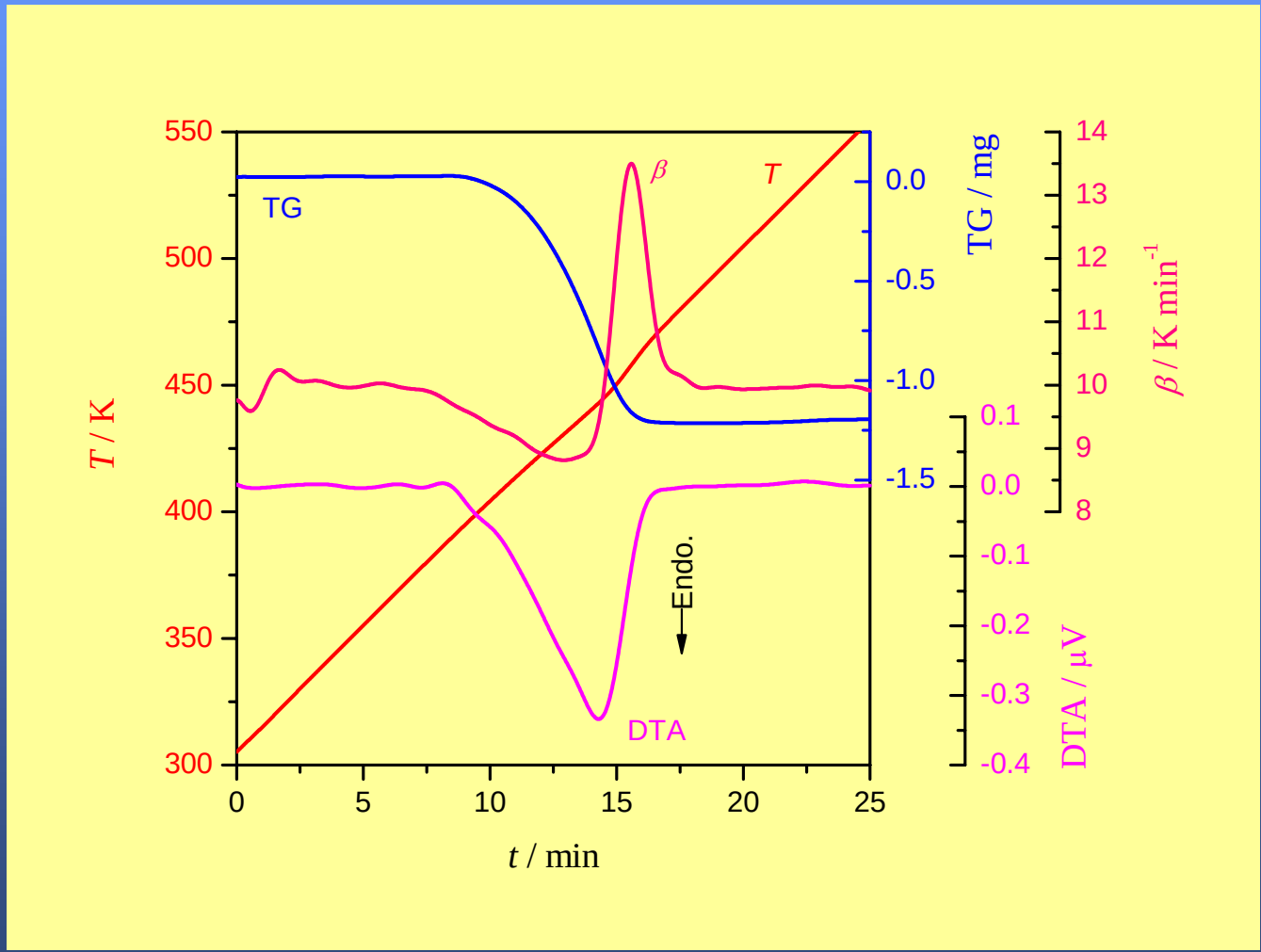
Ambiguities of TA Kinetics(1)

- Practical usefulness of the kinetic parameters? → Yes!!
  (1) For simulating the reaction process
  (2) For estimating life-time
  (3) Others
- Physico-chemical meaning of the kinetic parameters? → Not answered as yet!!

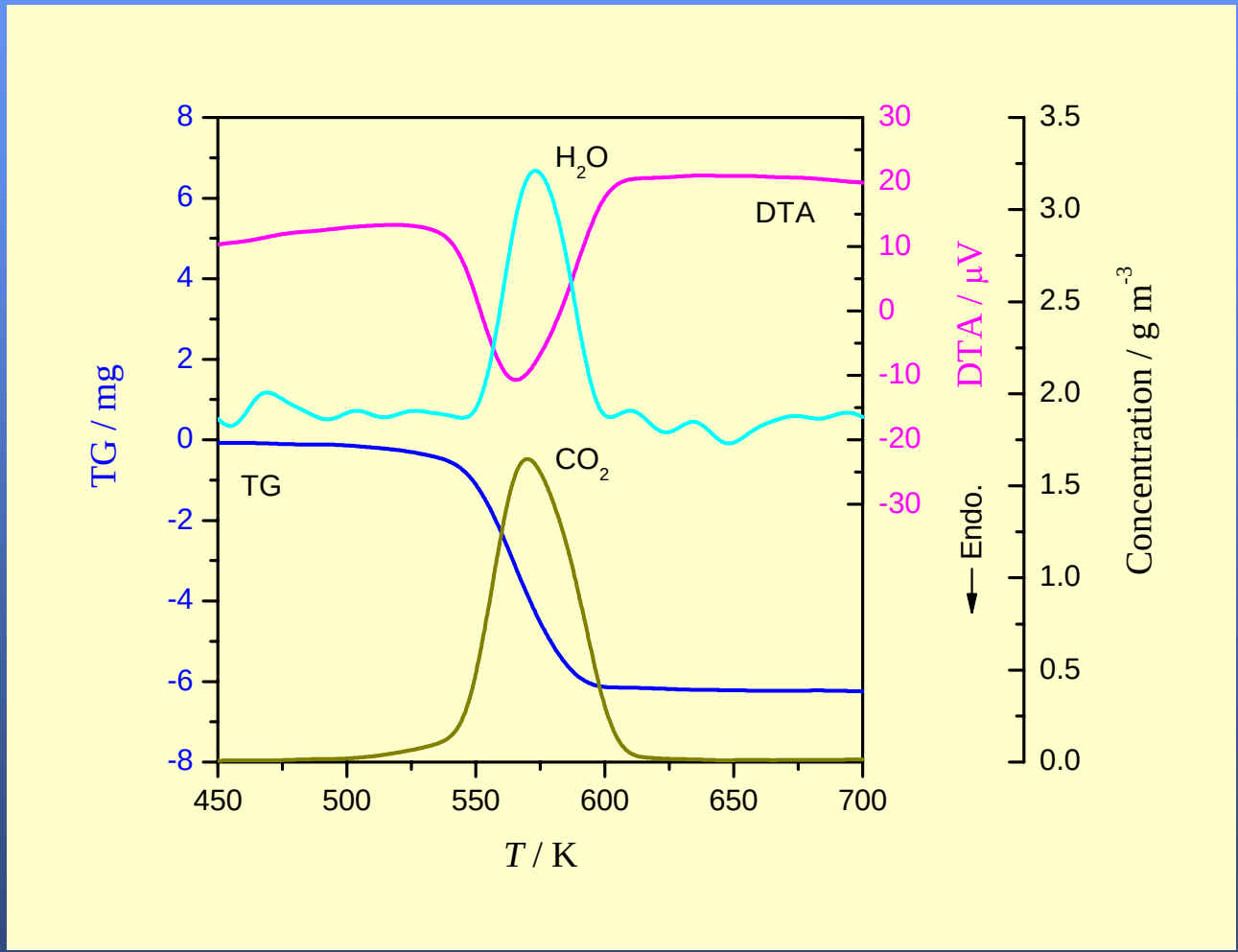
Problems

(1) Further detailed characterization of reaction mechanism
(2) Missing functional dependence in the idealized kinetic equation
(3) Reliability of the kinetic rate data measured by TA
    1) Self-cooling or self-heating effects
    2) Self-generated reaction atmosphere
    3) Mass-transfer and heat-transfer phenomena
    4) Others

Self-cooling effect



Self-generated atmosphere



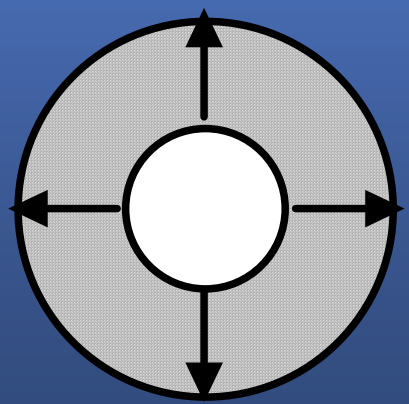
Ambiguities of TA kinetics(4)

Mass-transfere phenomena

Increase of Sample Mass

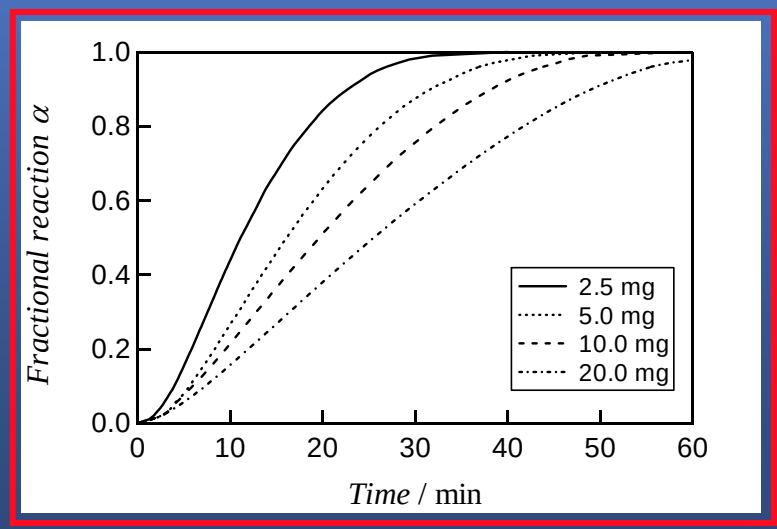
Balk or Pellet

Difficulty of internal diffusive escape of product gas through solid product layer

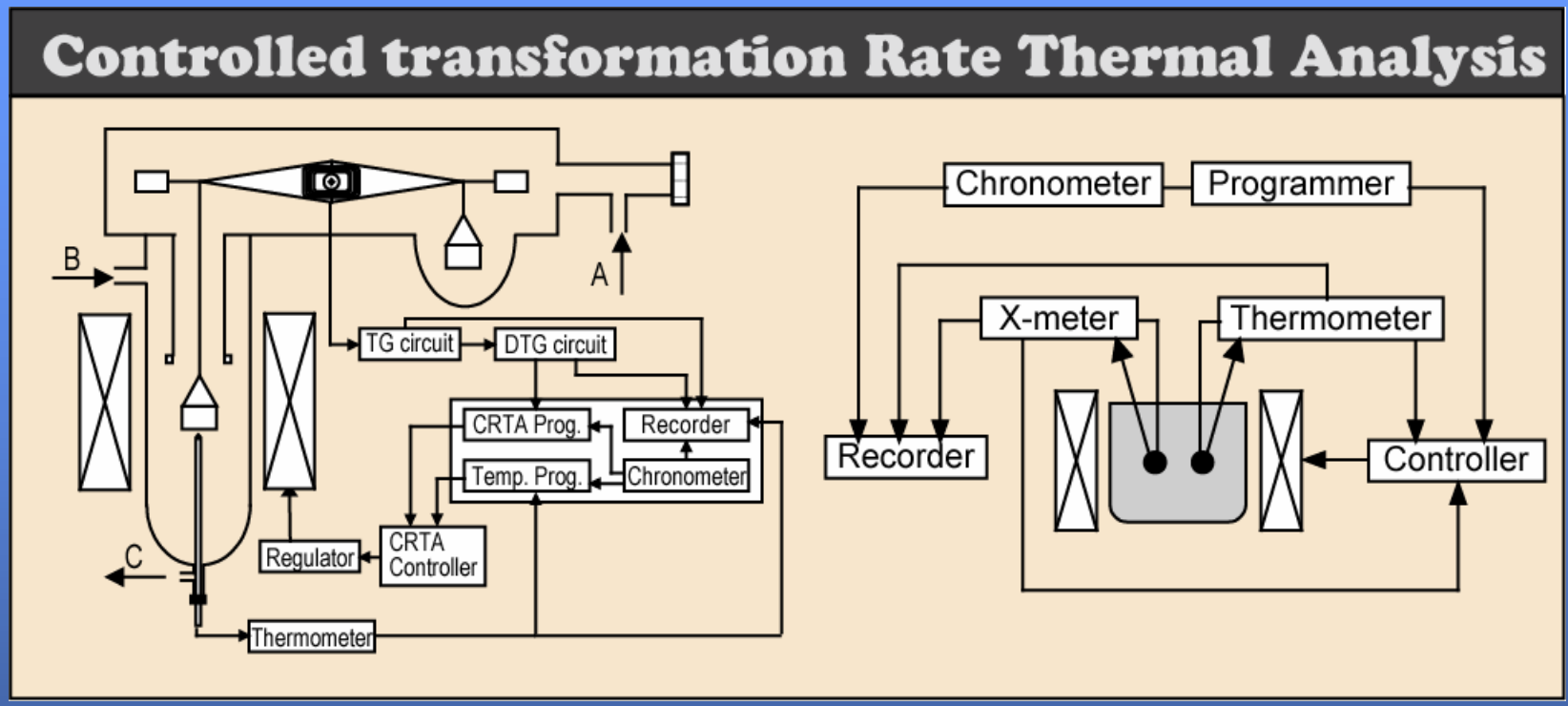


Powder

Difficulty of gross diffusion of product gas through sample power matrix



$Li_2SO_4 \cdot H_2O \rightarrow Li_2SO_4 + H_2O$



Practical Usefulness of CRTA Techniques

(1)Separation of overlapped reaction steps

(2)Measurement of kinetic rate data

(3)Process control and product control

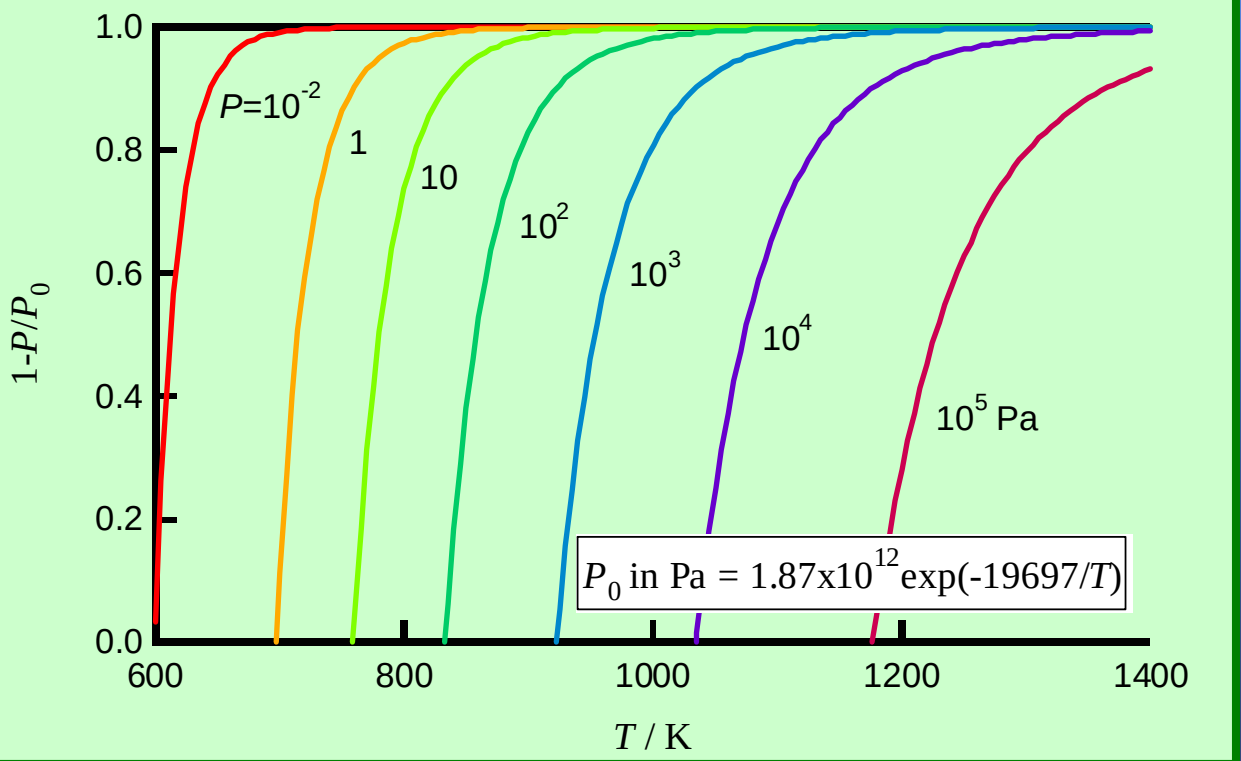
Technique	Feedback parameter
CRTG	Rate of mass change
CRDL	Rate of length change
CREGD	Rate of total gas evolution
CREGA	Rate of specific gas evolution

Thermal Decomposition of Calcite

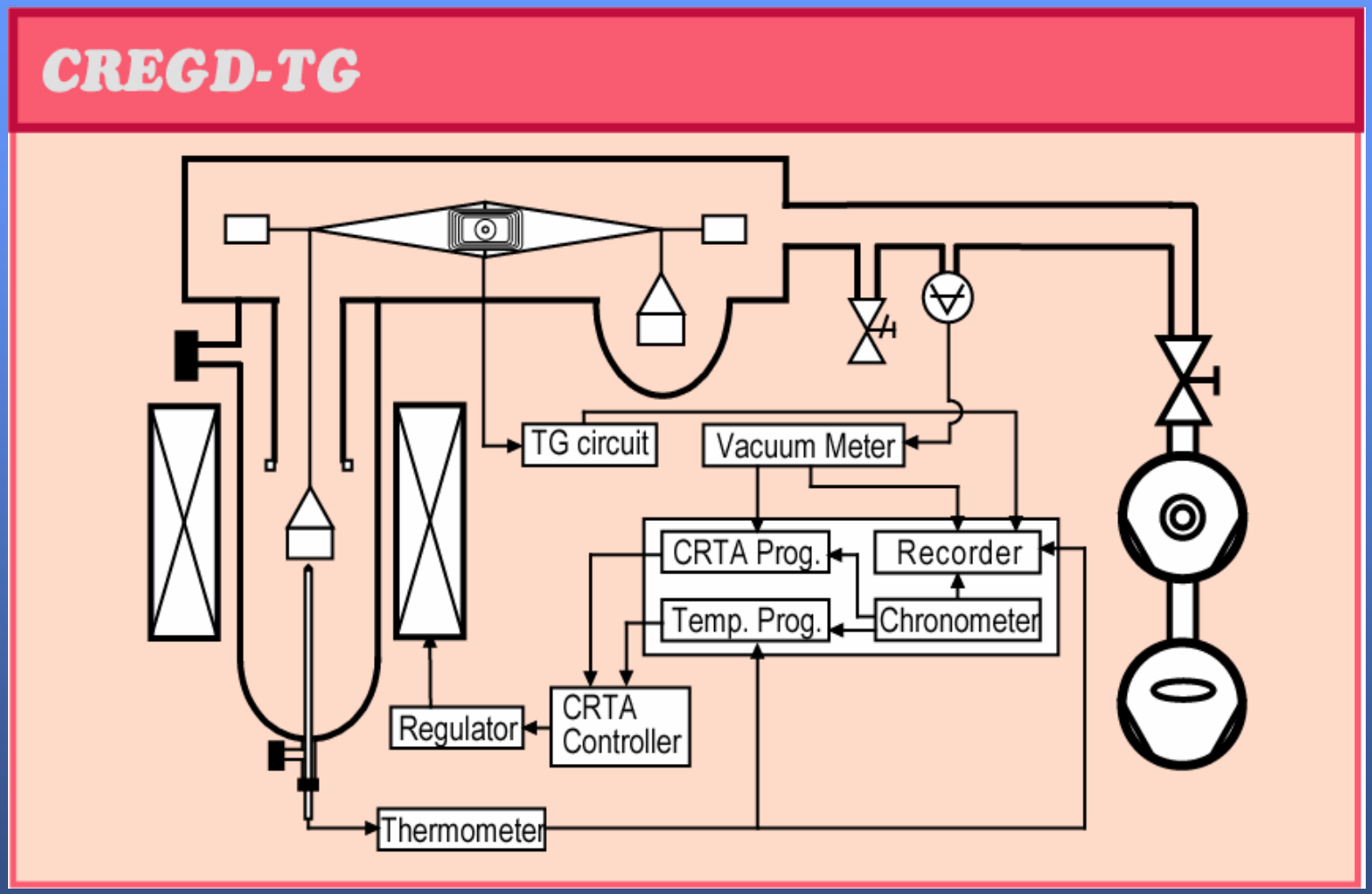
$CaCO_3 \rightarrow CaO + CO_2$

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right) f(\alpha)\left(1-\frac{P}{P_0}\right)$$

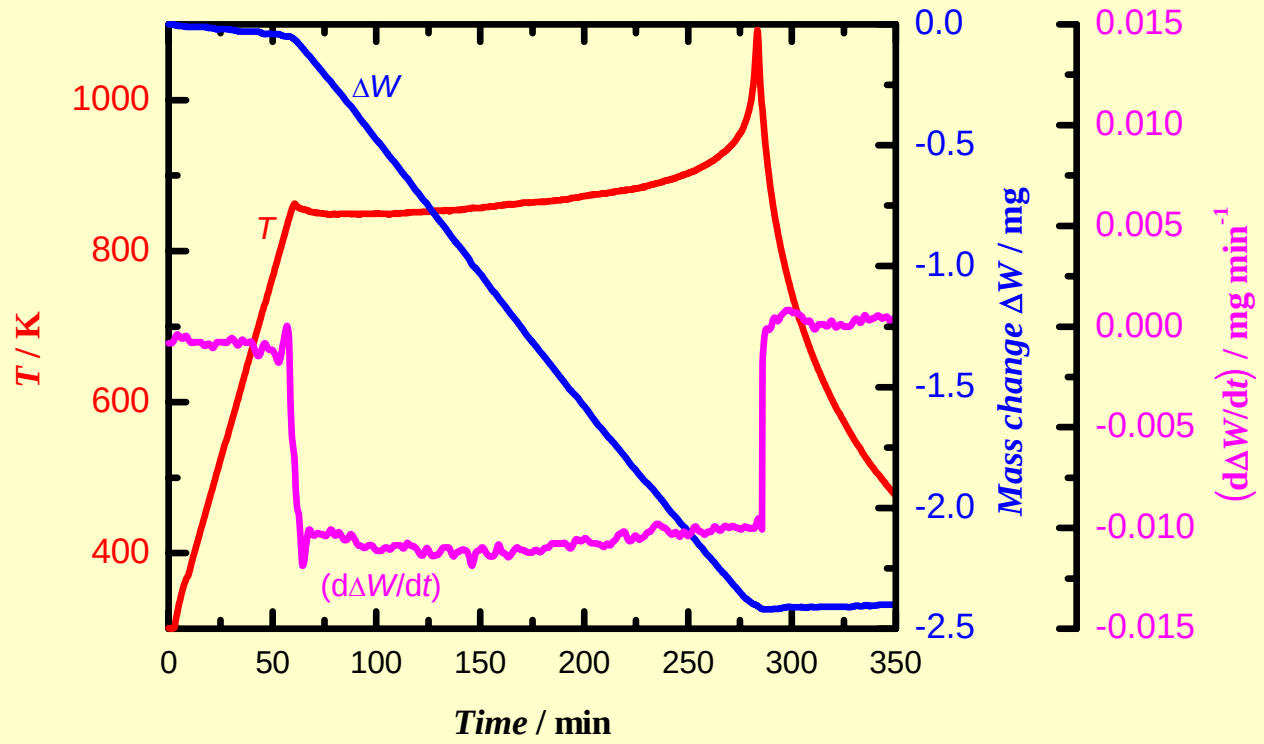
Temperature Dependence of $1-P/P_0$



CREGD-TG(2)


CREGD-TG
TG circuit
Vacuum Meter
CRTA Prog.
Recorder
Temp. Prog.
Chronometer
Regulator
CRTA Controller
Thermometer

Typical CREGD-TG Record



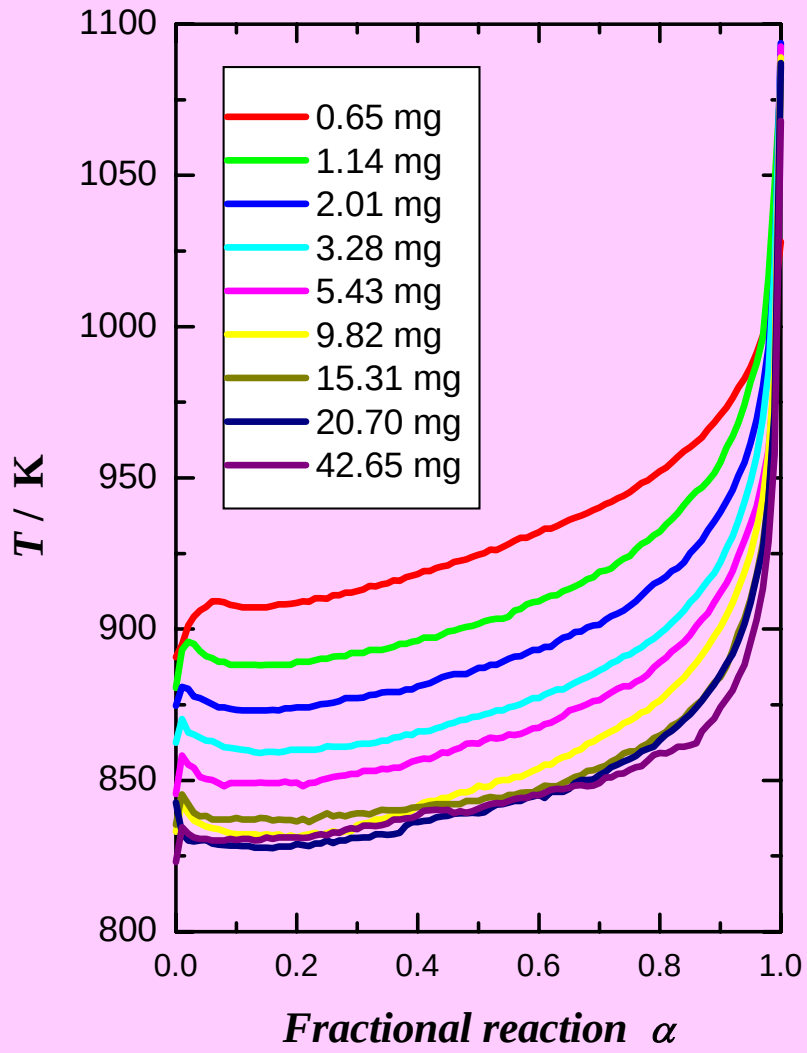
How to change decomposition rate for kinetic calculation?

(1)Control pressure

(2)Sample mass

(3)Basal pressure

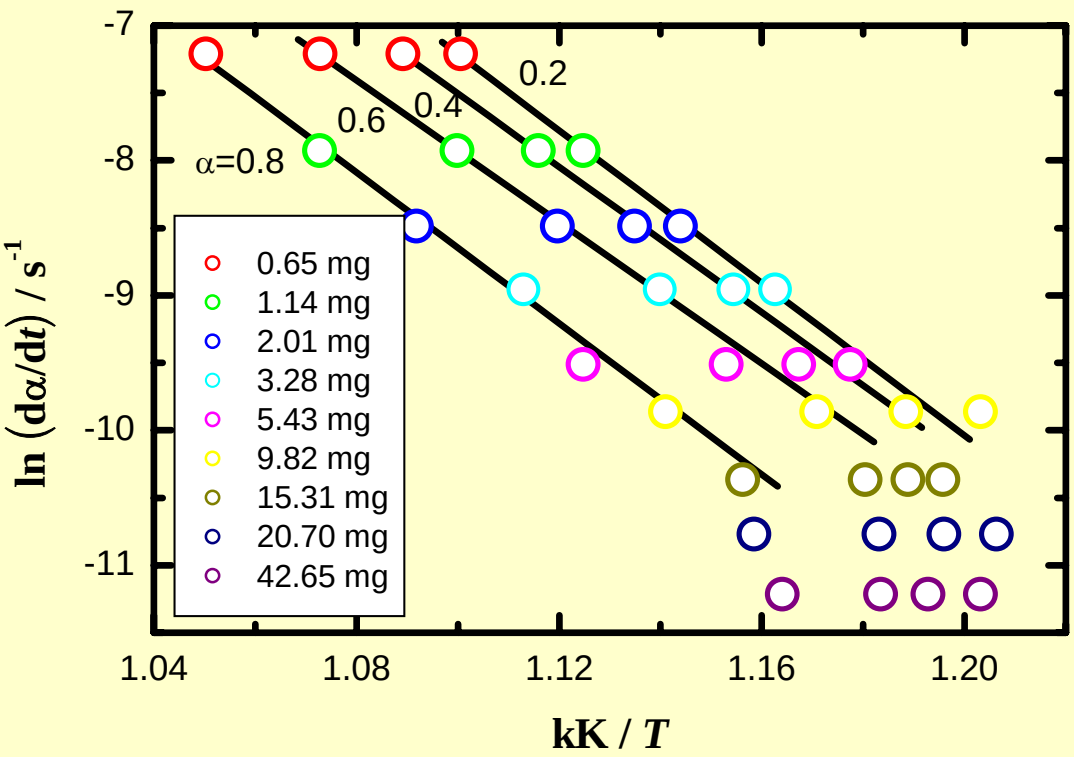
Effect of Sample Mass



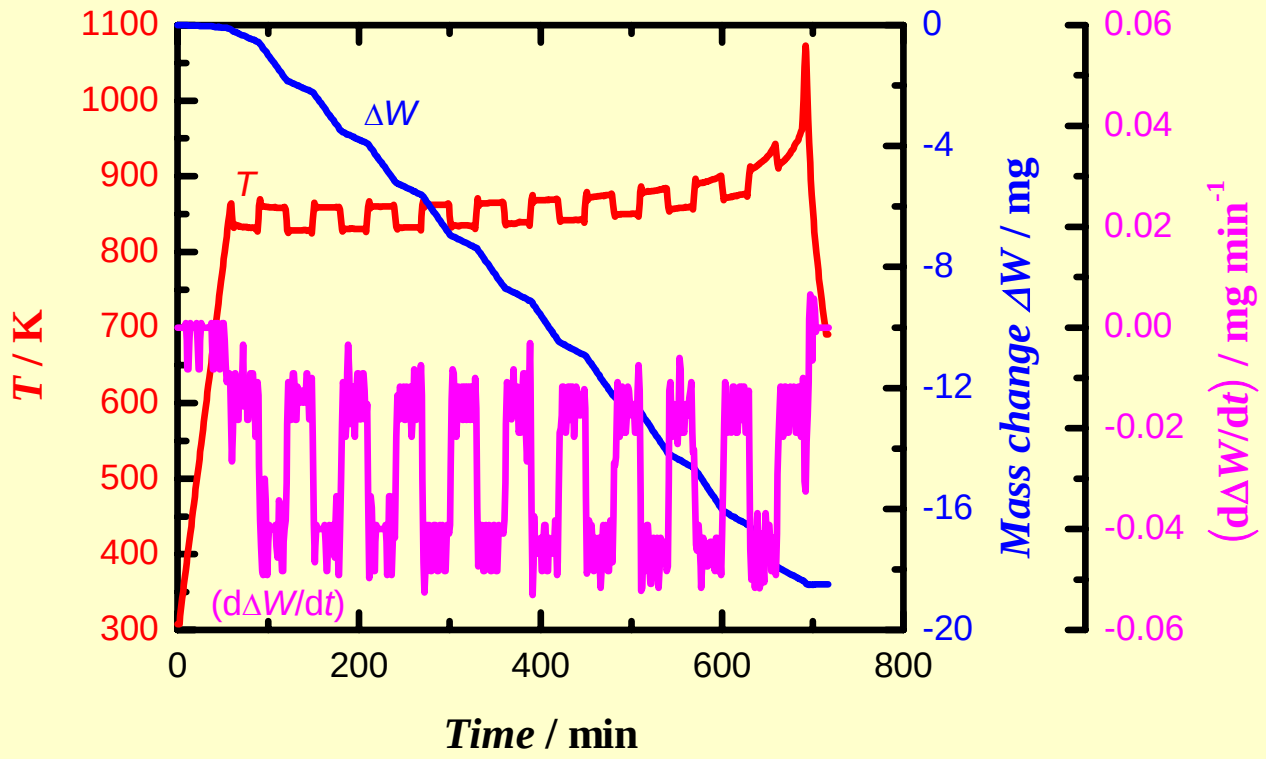
$$\left(1-\frac{P}{P_0}\right)\approx const.$$

$$\ln\left(\frac{d\alpha}{dt}\right)=\ln\left[Af(\alpha)\right]-\frac{E}{RT}$$

Friedman Plot

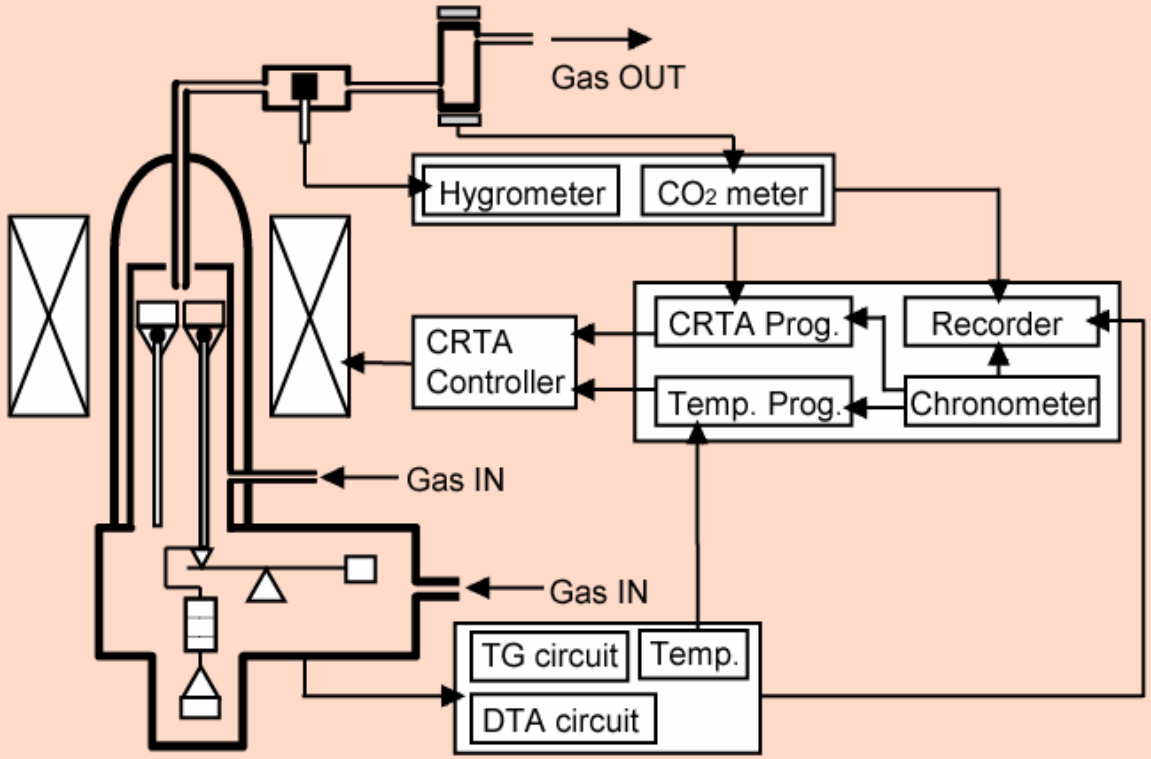


Typical Rate-jump CREGD-TG Record

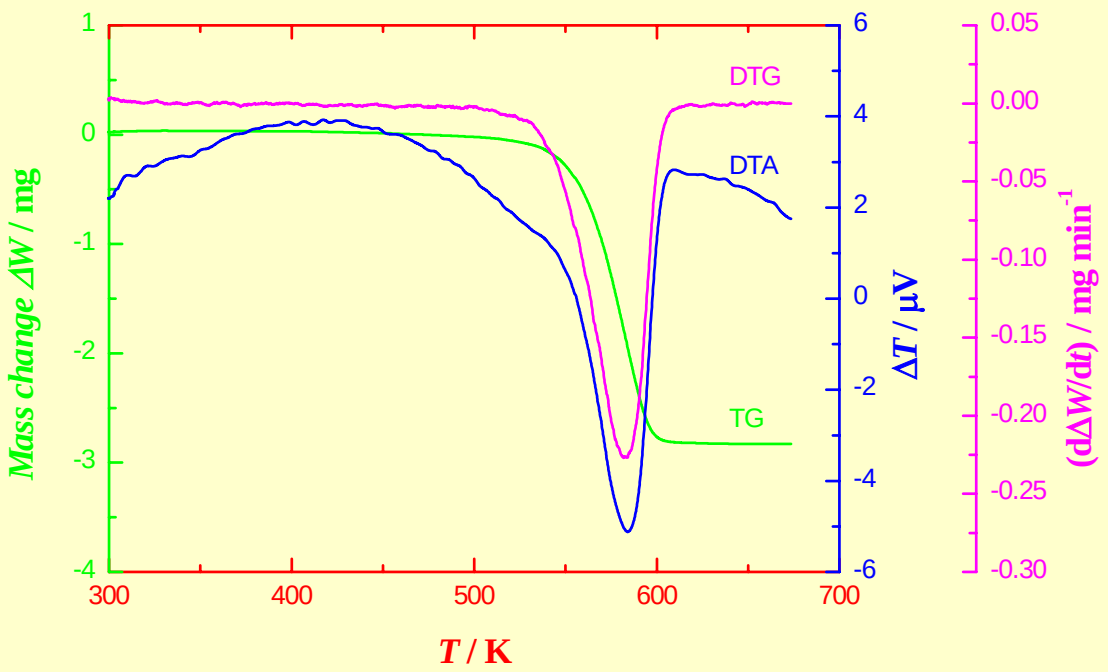


$$E = R\frac{T_1 T_2}{T_1 - T_2}\ln\frac{\left(\mathrm{d}\alpha/\mathrm{d}t\right)_1}{\left(\mathrm{d}\alpha/\mathrm{d}t\right)_2}$$

CREGA-TG


Gas OUT
Hygrometer
CO2 meter
CRTA Prog.
Recorder
CRTA Controller
Temp. Prog.
Chronometer
Gas IN
Gas IN
TG circuit
Temp.
DTA circuit

Thermal decomposition of synthetic malachite



$Cu_2CO_3(OH)_2 \rightarrow 2CuO + CO_2 \uparrow + H_2O \uparrow$

TG-DTA

☑Smooth

☑Single Step

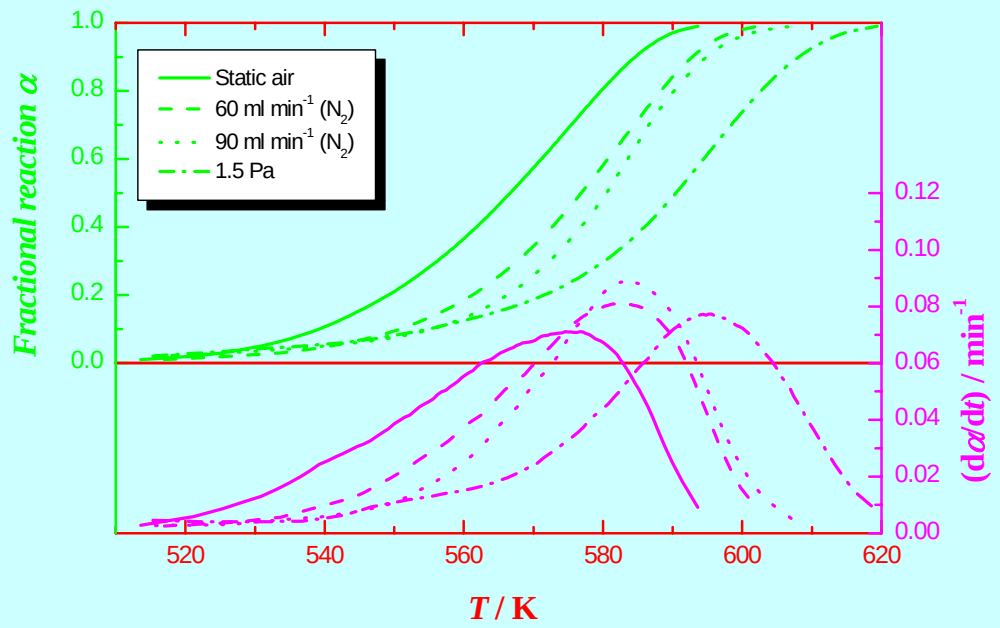
mass-lose process

Kinetics

$E \approx 190$ kJ mol^{-1}

First Order Reaction

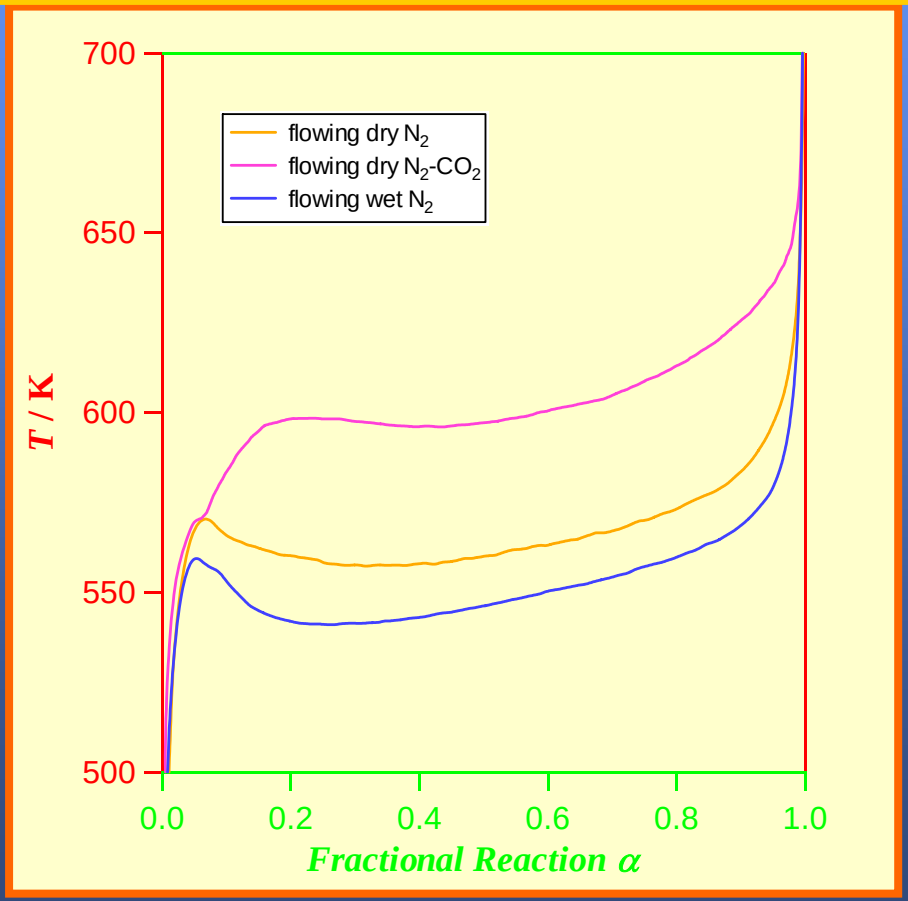
Influence of Reaction Atmosphere



With increasing the influence of self-generated atmospheric condition

Reaction temperature shifts systematically to lower temperature region

Influence of atmospheric CO_2 and H_2O



Dry N_2-CO_2

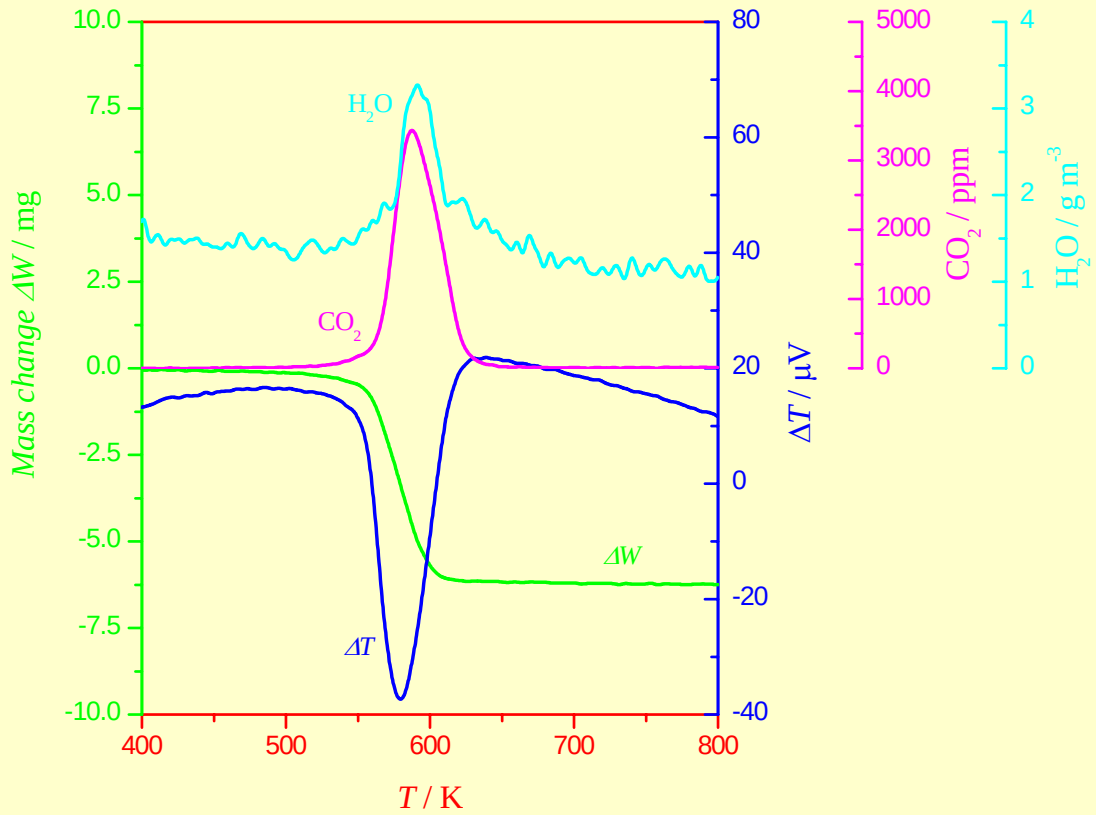
Normal

Dry N_2

Inverse

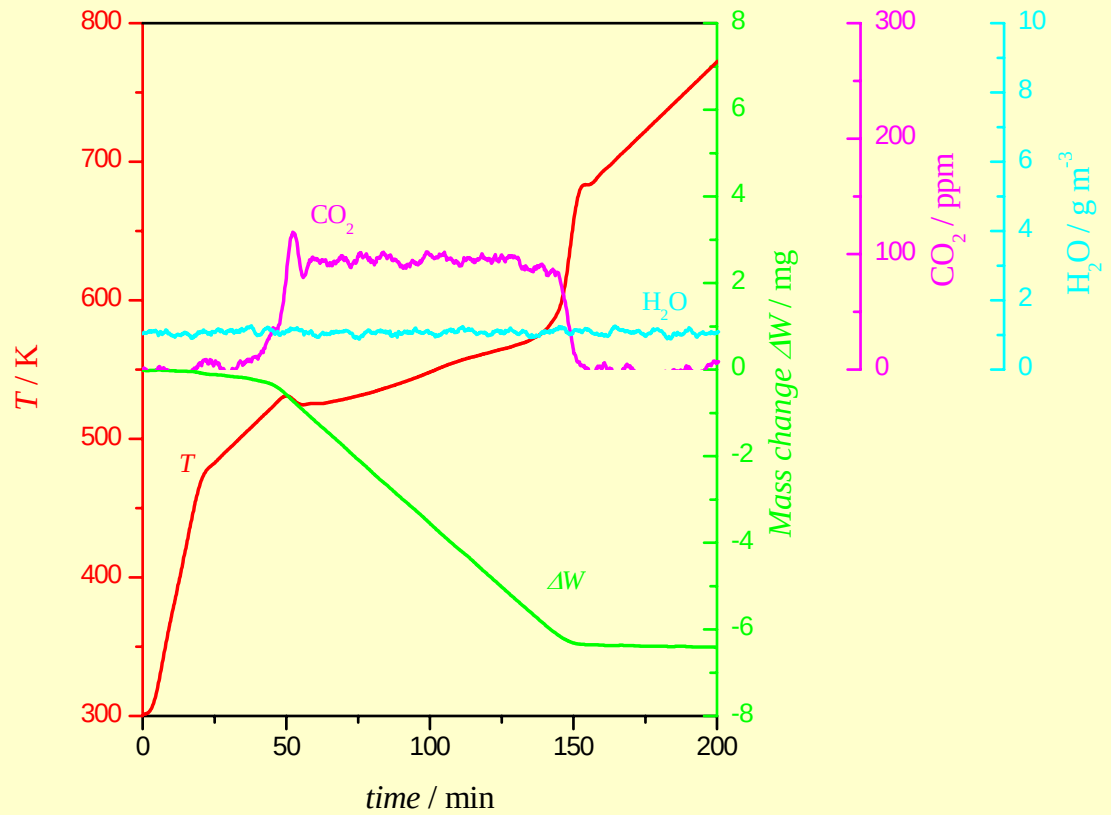
Wet N_2

A Typical TG-DTA-EGA Curves



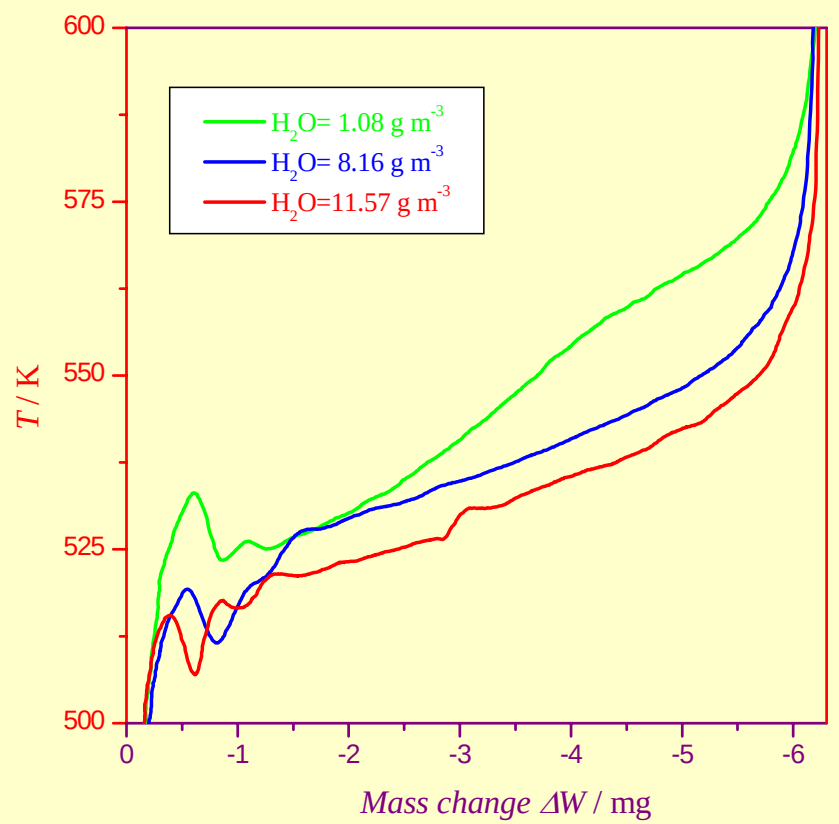
Sample mass:
20.08 mg
Carrier Gas:
dry N_2
Flow Rate:
200 ml min^{-1}
H.R.:
10.0 K min^{-1}

Typical CREGA(CO_2)-TG Curves



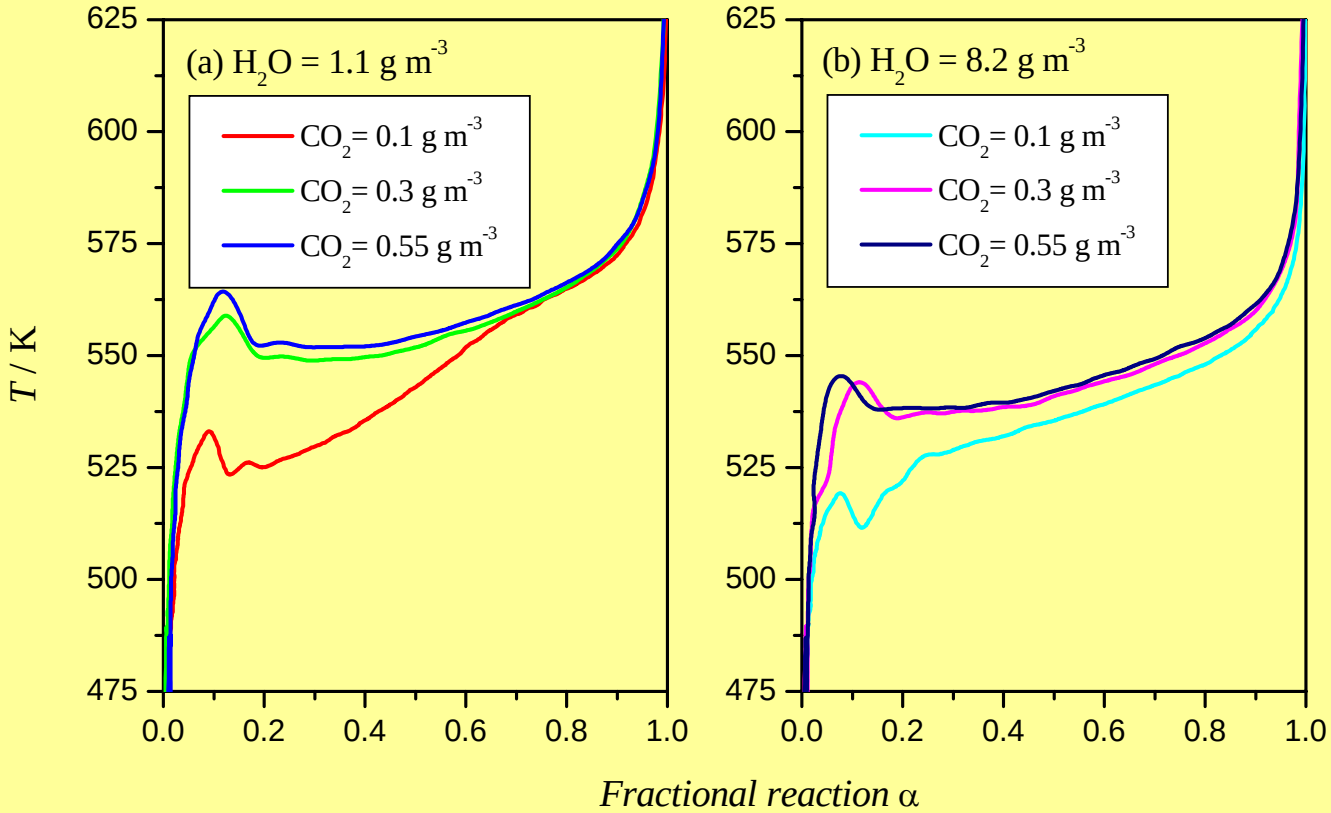
Sample mass:
20.55 mg
Carrier Gas:
dry N_2
Flow Rate:
200 ml min^{-1}
H.R.:
2.0 K min^{-1}
Controlled Gas:
CO_2 (100ppm)

Influence of Water Vapor



Sample mass: 20.55 mg
Carrier Gas: N_2
with H_2O: 1.98 g m^{-3}
8.14 g m^{-3}
11.57 g m^{-3}
Flow Rate: 200 ml min^{-1}
H.R.: 2.0 K min^{-1}
Controlled Gas: CO_2
Controlled Value: 100ppm

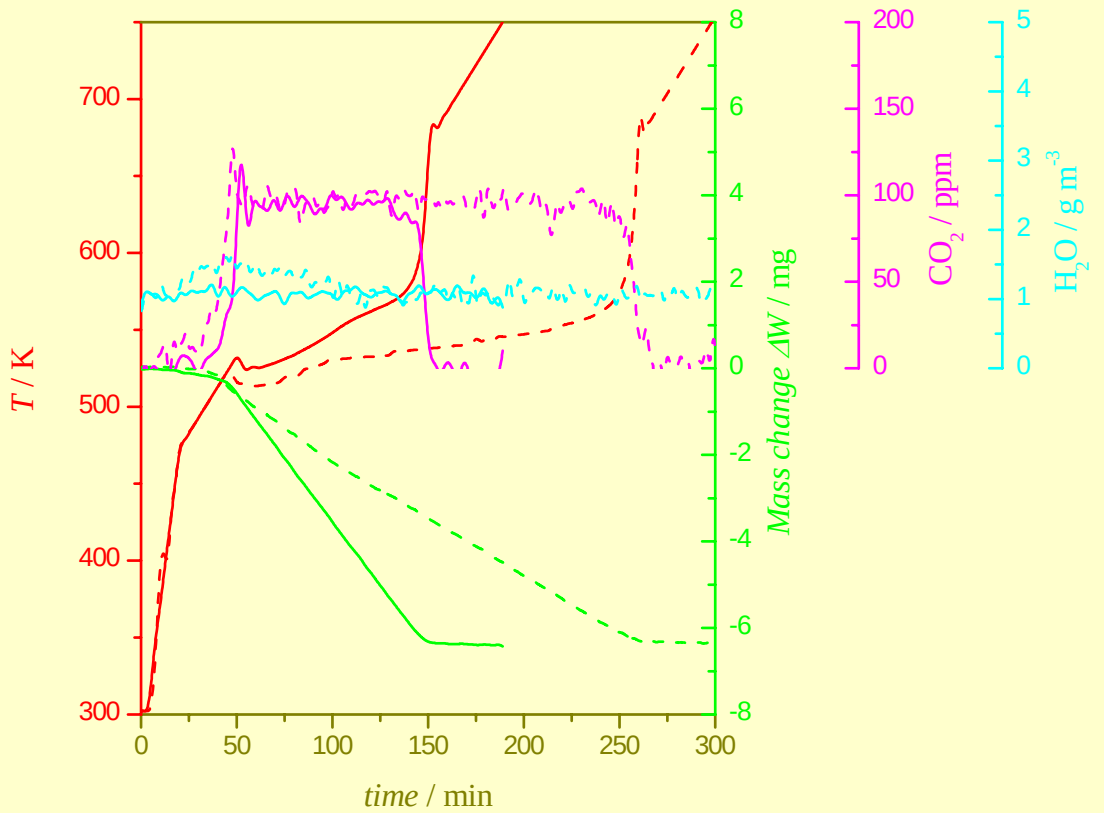
Influence of CO_2



How to change decomposition rate for kinetic calculation?

Parameter	Problem
Control Value	Change in the partial pressure of evolved gas
Sample Mass	Change in the mass-transfer phenomena in the sample matrix
Flow Rate	Change in the suction effect

Two Different CREGA(CO_2)-TG Curves for Kinetic Calculation

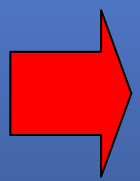


Sample Mass:
20.22 mg
Ref. Mass:
20.20 mg
Carrier Gas:
dry N_2
Flow Rate:
200 ml min^{-1}
H.R.:
2.0 K min^{-1}
Controlled Gas:
CO_2 (100ppm)

Conclusion(1)

Thermal Decomposition of Solids

Application of Dynamic Temperature Change in the Type of Feedback Control



Possibility of Quantitative Control of the Relationship between Reaction Kinetics and Self-generated Reaction Atmosphere

Near-equilibrium  Far-equilibrium

Logical Consideration on Kinetic Characteristics

⇒ Appropriate Control of Reaction Atmosphere and Reaction Rate

⇓

Practical Usefulness of CRTA Techniques

(1)Separation of overlapped reaction steps

(2)Measurement of kinetic rate data

(3)Process control and product control

The End