Solid State Kinetics

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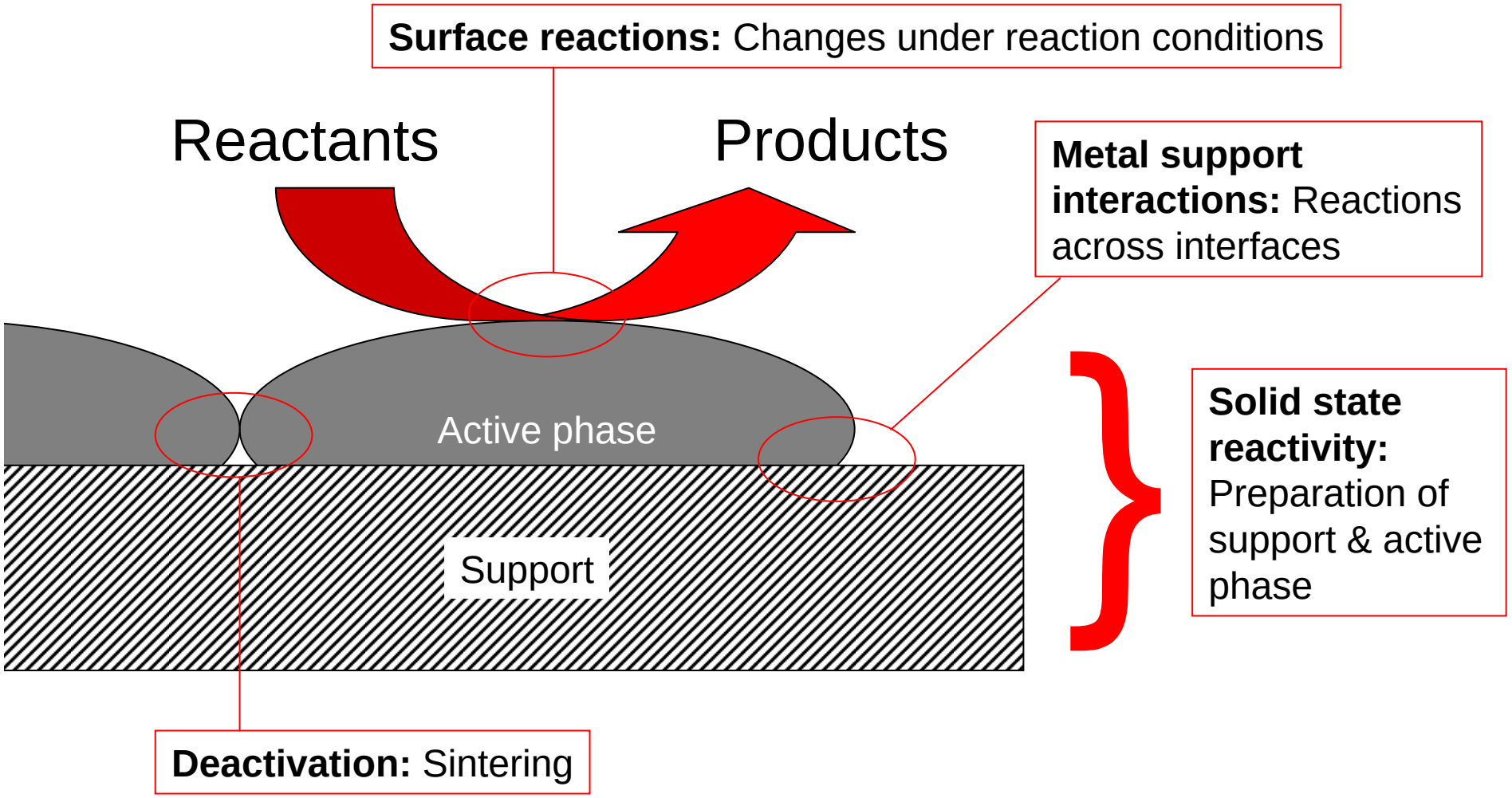
Solid State Processes in Catalysis



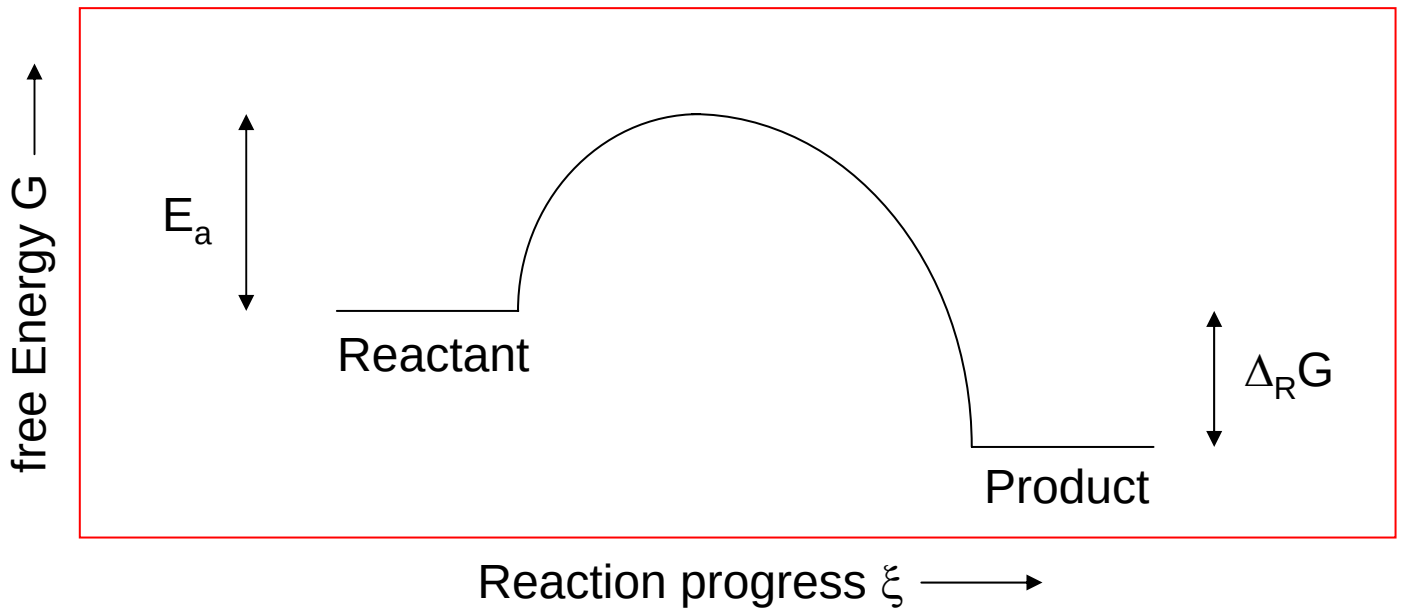
Outline

- I. Fundamentals of kinetics
- II. Solids are special: Diffusion, Defects, Models
- III. Reactivity of solids
  - a. decomposition reactions, sintering
  - b. solid-gas reactions
  - c. solid-solid reactions
  - d. solid-liquid reactions
- IV. Examples
- V. Summary
- VI. Critical review

I. Fundamentals: Kinetics vs. Thermodynamics

- Thermodynamics: Is a reaction favoured? ($\Delta G < 0$)
  - Diamond should transform to graphite at ambient pressure

- Kinetics: How fast is a reaction?
  - Diamond → graphite is kinetically hindered (extremely slow) and not observed at room temperature



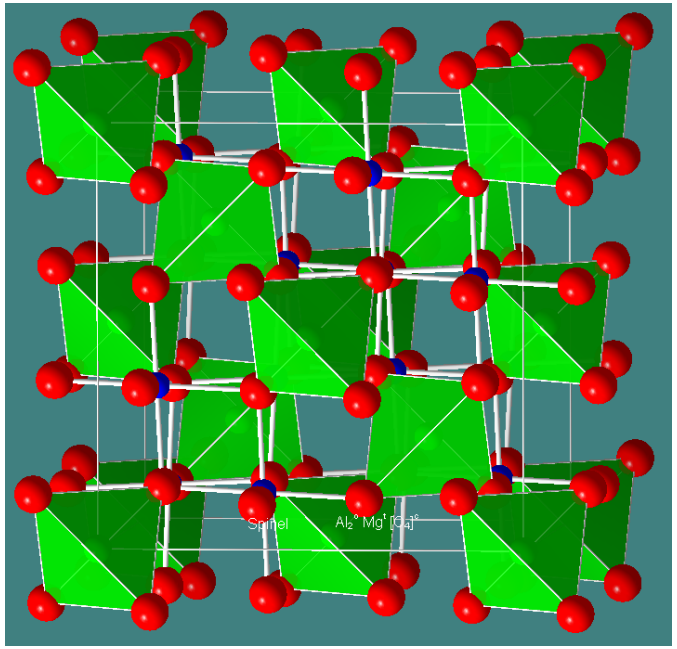
I. Fundamentals: Definitions

- Activation Energy:
  - Height of energy barrier between reactant and activated complex
- Reaction rate: $$r = \frac{1}{V}\frac{d\xi}{dt} = \frac{1}{\nu_i}\frac{dc_i}{dt}$$
- Rate law: $$r = k \cdot c_i^a \cdot c_j^b \cdot \ldots$$ rate constant k
  reaction order n = a + b
- T-dependence: $$k(T) = A \cdot e^{-\frac{E_a}{RT}}$$ Arrhenius
- Reaction mechanism:
  - System of consecutive or competing elementary reactions
- Rate limiting step

II. Solids: The crystal lattice

- "Immobility" of atoms in solids

- General reaction steps of heterogeneous reactions:
  - Diffusion of reactant to reactive interface
  - Adsorption at interface (Desorption for decomposition)
  - Reaction on atomic scale at the interface
  - Nucleation of product and growth
  - Diffusion of products away from the reactive interface



- Transport phenomena (diffusion, heat) involved in heterogeneous reactions

- Reaction zone confined: Average concentration of reactant is only of little significance in solid state reactions
  → homogeneous reaction kinetics $r = -k[\text{Reactant}]^n$ do not apply!

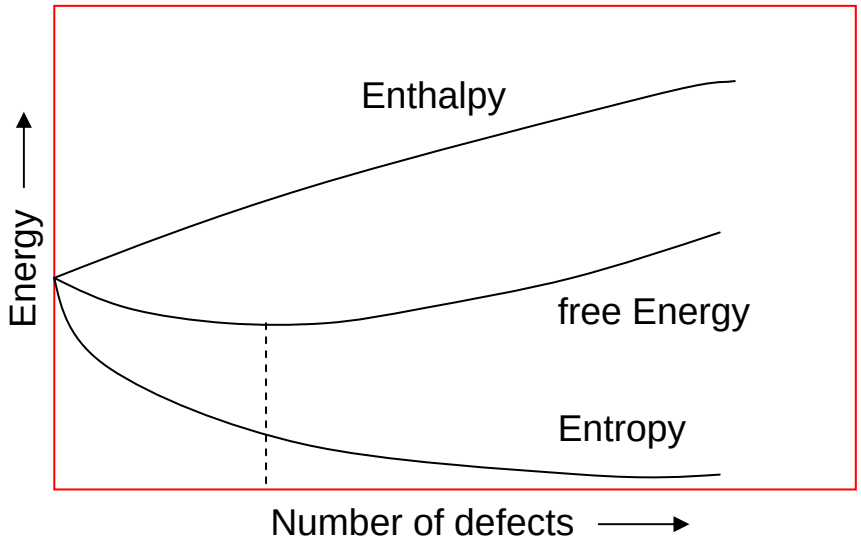
II. Solids: Considerations for solid state preparation

- Diffusion often is the rate limiting step in solid state reactions

- Solid state synthesis requires
  - high temperatures: Ceramic method
    - usually thermodynamically stable or even inert products
    - dense materials of low surface area
  - special low-T preparation method: Soft Chemistry
    - kinetically stabilized products
    - open framework or porous materials
    - e.g. CVD, Hydrothermal synthesis, Sol-gel, molten flux, …

II. Solids: Defects

- Defects play a crucial role for the transport properties of a solid (also for many other properties like mechanical, electronic, optical, …)
- Ideal structure (perfect crystal) vs. real structure (defective crystal)
  - Thermodynamics of defects: $\Delta G = \Delta H - T\Delta S$

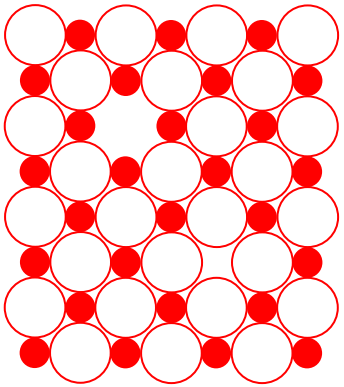


- ~ 10 000 vacancies in 1 mole NaCl (at RT)

II. Solids: Defects

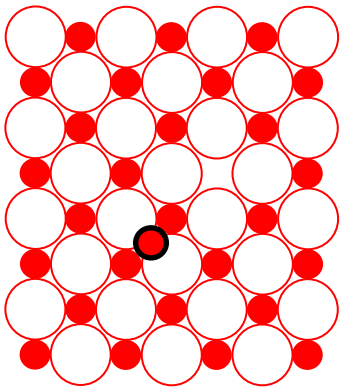
- Intrinsic point defects:
  - Schottky defect
    (pairs of ions)

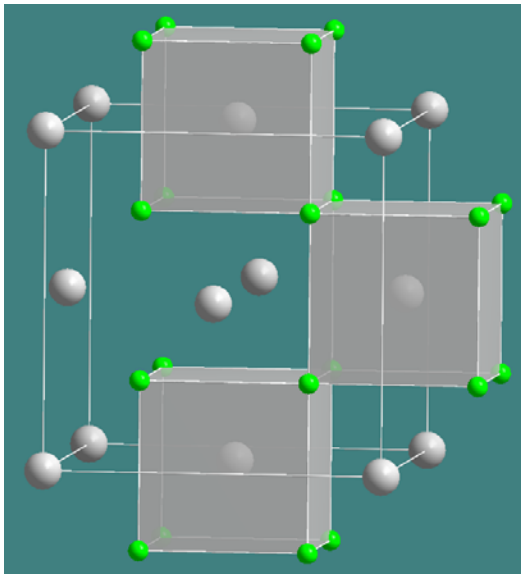
    NaCl: $V_{Na}^{-} + V_{Cl}^{+}$



  - Frenkel defect
    (ion on interstitial site)

    AgBr:
    $Ag_{Ag} \rightarrow Ag_{i}^{+} + V_{Ag}^{-}$





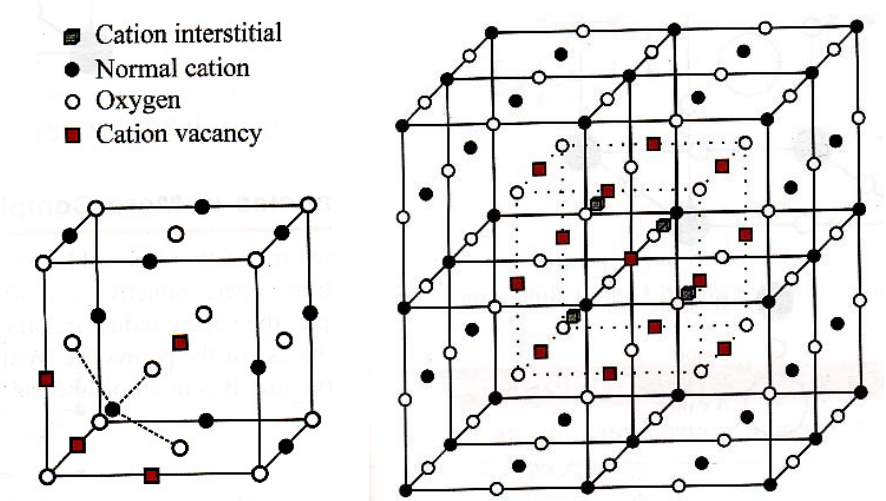
usually cationic sublattice, exception CaF_2-type compounds like ZrO_2

II. Solids: Defects

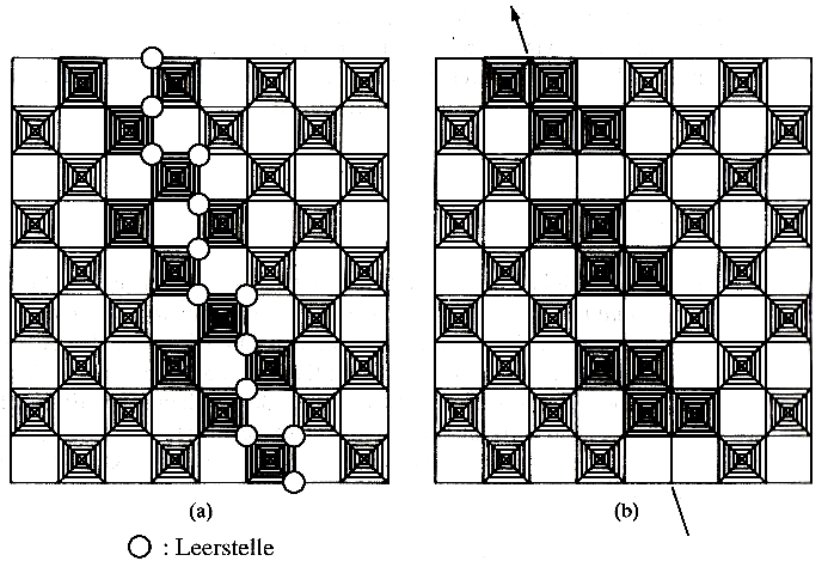
- Extrinsic defects: Non-stochiometry, doping
  - $Fe_{1-x}O$: Cation vacancies
  - ZnO_{1-x}: Zn^{2+} on interstitial sites

- Clustering of defect, randomly (e.g. Koch-Cohen clusters) or ordered (e.g. crystallographic shear)

S. Dann (2000)



Interstitial cation in tetrahedral void "blocks" neighbouring octaheral voids (e.g. FeO)



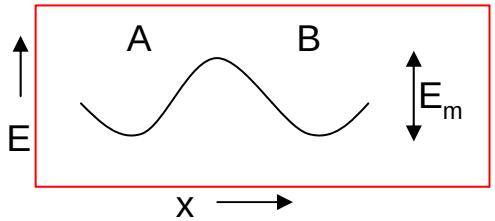
L. Smart, E. Moore (1997)

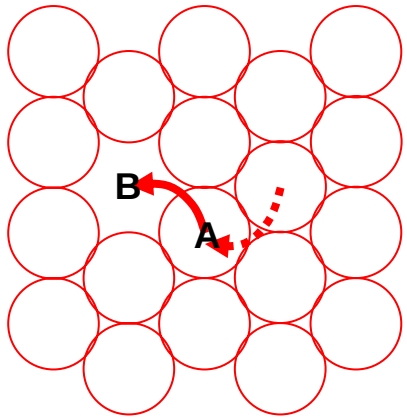
Vacancies order and enable crystallographic shear e.g. in WO_{3-x}

II. Solids: Diffusion

- Point defects are mobile in the lattice at sufficient temperatures and enable "atomic jumps"

$$r = \bar{\nu} \cdot e^{-\frac{E_m}{kT}}$$





- Dislocations, grain boundaries and surfaces are favourable migration paths

- Atoms are in a state of continual migration within the solid

- Diffusion: Mass transport levelling out variations in composition

$$J = -D\frac{dc}{dx} \qquad \text{(Fick's 1st law)}$$

Net mass flow proportional to concentration gradient
D_i: Diffusion coefficient (dimension: m^2s^{-1})

II. Solids: Diffusion

- N diffusing components: Generalisation of Fick's law

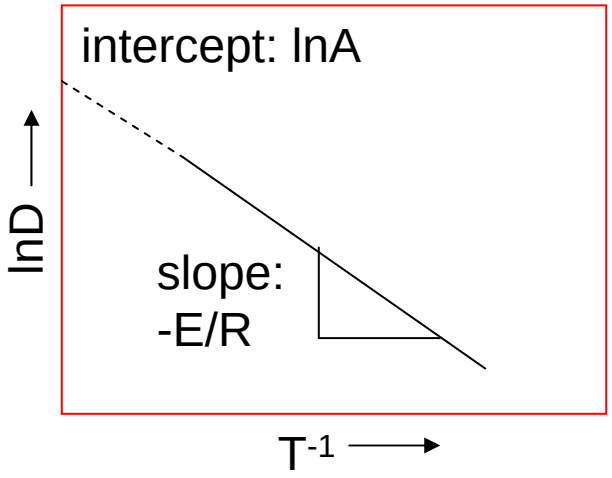
$$J_i = \sum_{j=1}^{N} D_{ij} \frac{dc_j}{dx}$$

Dij: chemical diffusion coefficient

- Temperature dependence of D:

$$D = A \cdot e^{-\frac{E}{RT}}$$

(Arrhenius)



- Graphical evaluation:

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

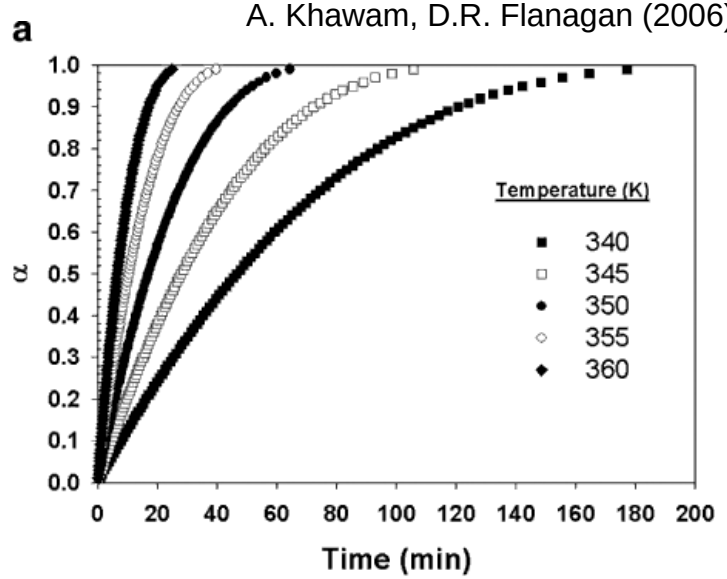
- linear behaviour: single migration mechanism assumed
- deviation from linear behaviour attributed to more than one mechanism

II. Solids: Methods in solid state kinetics

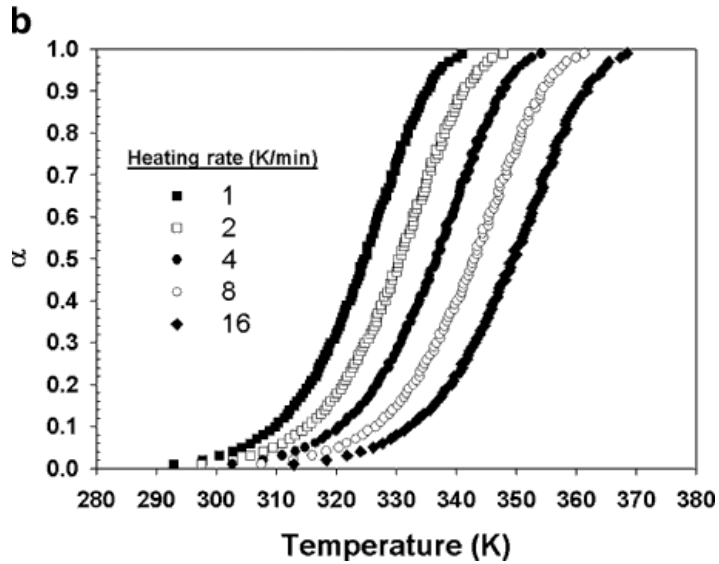
- Measurement of the extent of reaction α (dimensionless) as a function of time and temperature under either isothermal or temperature-controlled conditions

A. Khawam, D.R. Flanagan (2006)

isothermal



non-isothermal
(constant heating rate)



II. Solids: Methods in solid state kinetics

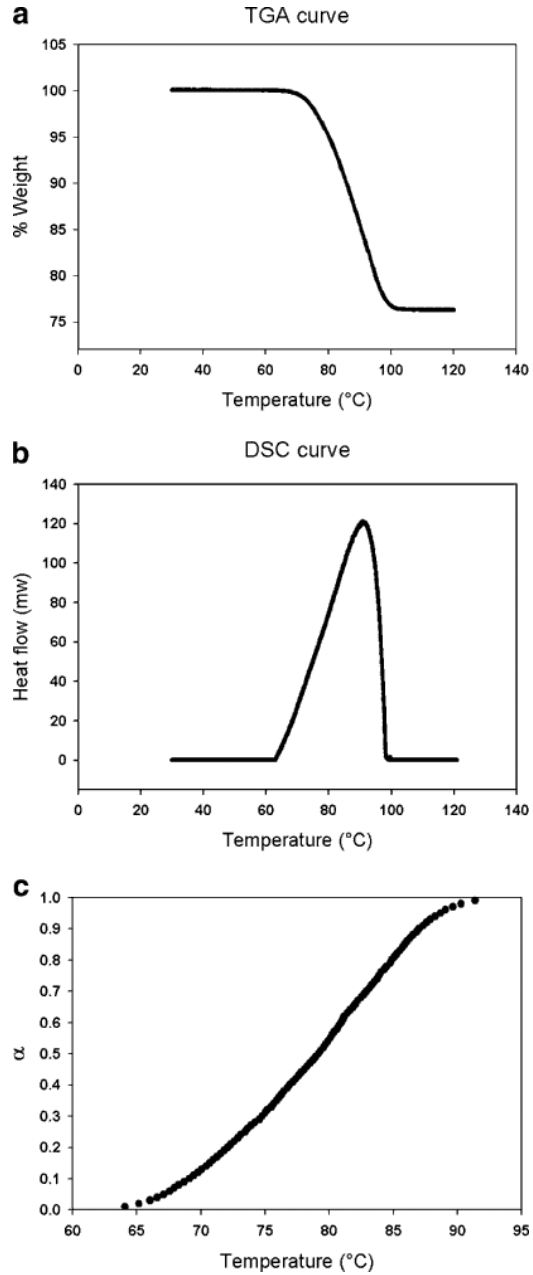
- Several observables suitable (any experimental method probing product formation at sufficient accuracy and time resolution):
  - mass loss (TGA)
  - heat flow (DTA, DSC)
  - time-resolved features in XRD, XANES, FTIR, Raman, …

- Calculation of α for TGA:
  - isothermal experiment:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_{final}}$$

  - linear heating rate:

$$\alpha = \frac{m_0 - m_T}{m_0 - m_{final}}$$



A. Khawam, D.R. Flanagan (2006)

II. Solids: Evaluation

- Formal kinetic (gas phase) for unimolecular elementary reaction (n=1):

$$r = \frac{d[\text{Reactant}]}{\text{dt}} = -k[\text{Reactant}] \qquad -\ln\frac{[\text{Reactant}]}{[\text{Reactant}]_0} = kt$$

- For solid state reactions:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \qquad \boxed{g(\alpha) = kt}$$

integral reaction model

- Models describe the reaction and can be converted into a mathematical expression

II. Solids: Models

- Several models for solid state reactions exist

- Models are classified by the underlying assumptions:
  - Nucleation: Formation and growth of nuclei are considered to be rate-limiting. Nucleation rate is different from the growth rate and the model accounts for both
  - Geometrical contraction: The progress of the product layer from the surface to the inner crystal is considered to be rate-limiting. It is different for various crystal morphologies (cubic, cylindrical, spherical, …)
  - Diffusion: Diffusion of reactant or product is considered to be rate-limiting.
  - Reaction order: The rate law is based on considerations for homogeneous kinetics

II. Solids: Models

Table 1. Solid-State Rate Expressions for Different Reaction Models, Shapes of These Models Is Given in Figure 3

Model		Differential Form[a] $f(\alpha) = \frac{1}{k}\frac{d\alpha}{dt}$	Integral Form[a] $g(\alpha) = kt$
Nucleation models			
Power law (P2)		$2\ \alpha^{(1/2)}$	$\alpha^{(1/2)}$
Power law (P3)		$3\ \alpha^{(2/3)}$	$\alpha^{(1/3)}$
Power law (P4)	*m*	$4\ \alpha^{(3/4)}$	$\alpha^{(1/4)}$
Avarami-Erofe'ev (A2)	2.00	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
Avarami-Erofe'ev (A3)	3.00	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
Avarami-Erofe'ev (A4)		$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
Prout–Tompkins (B1)		$\alpha\ (1-\alpha)$	$\ln[\alpha/(1-\alpha)]$
Geometrical Contraction models			
Contracting area (R2)	1.04	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]$
Contracting volume (R3)	1.08	$3(1-\alpha)^{2/3}$	$[1-(1-\alpha)^{1/3}]$
Diffusion models			
1-D diffusion (D1)	0.62	$1/2\alpha$	α^2
2-D diffusion (D2)		$[-\ln(1-\alpha)]^{-1}$	$[(1-\alpha)\ln(1-\alpha)]+\alpha$
3-D diffusion-Jander eqn.(D3)	0.57	$3(1-\alpha)^{2/3}/2(1-(1-\alpha)^{1/3})$	$[1-(1-\alpha)^{1/3}]^2$
Ginstling–Brounshtein (D4)		$(3/2((1-\alpha)^{-1/3}-1)$	$1-(2\alpha/3)-(1-\alpha)^{2/3}$
Reaction-order models			
Zero-order (F0/R1)		1	α
First-order (F1)		$(1-\alpha)$	$-\ln(1-\alpha)$
Second-order (F2)		$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
Third-order (F3)		$(1-\alpha)^3$	$0.5\ ((1-\alpha)^{-2}-1)$

[a]In some references f(α) and g(α) have opposite designations.

A. Khawam, D.R. Flanagan (2006)

- General expression for isothermal reactions (lnln-method, Sharp-Hancock)

$$\ln[-\ln(1-\alpha)] = m \cdot \ln(k) + m \cdot \ln(t)$$

plot ln[-ln(1-a)] vs. ln(t)

  - parts of the reaction which follow the same mechanism give straight lines
  - k and m can be derived from the slope and intercept of the Sharp-Hancock plot

II. Solids: Models

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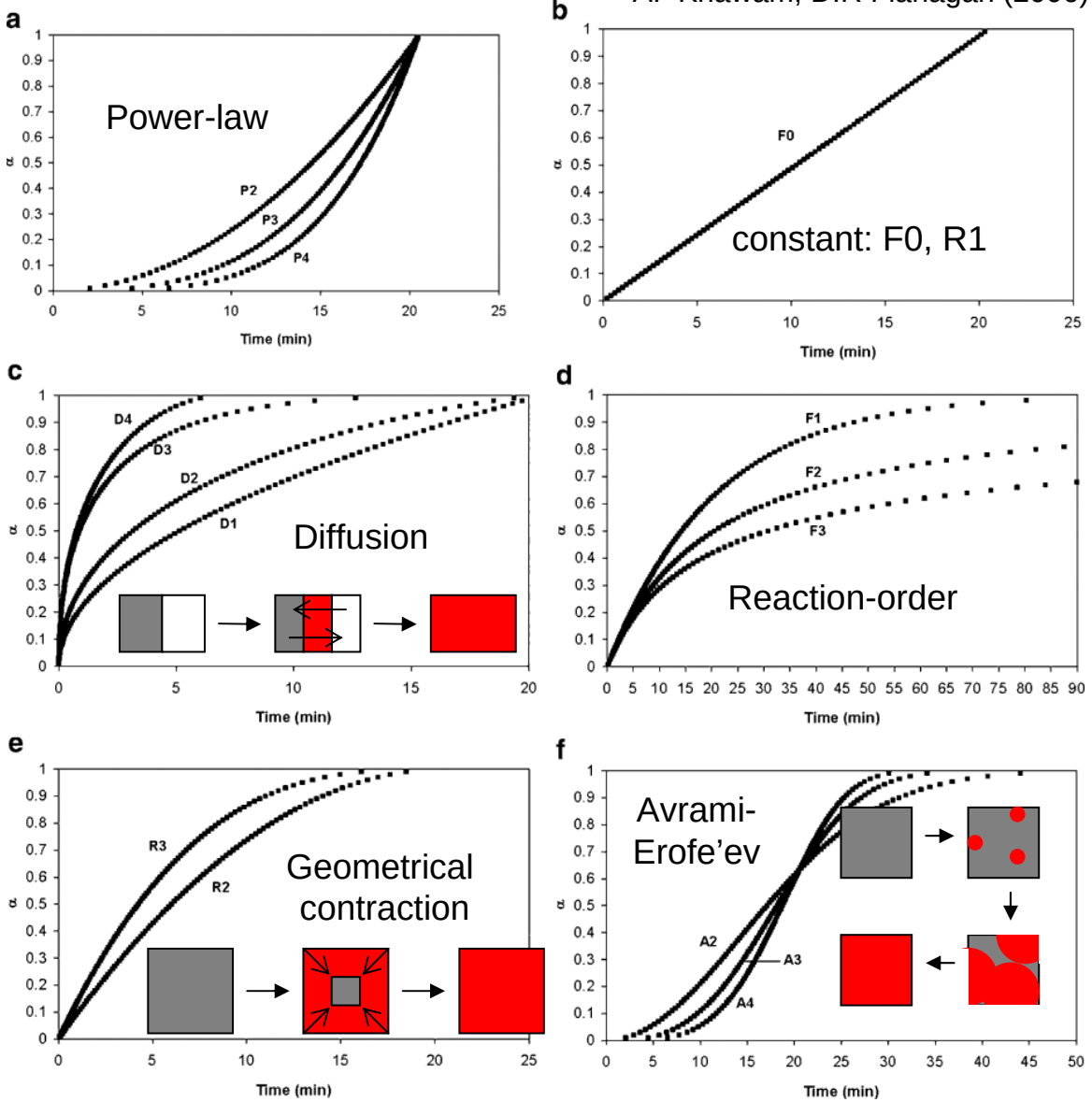
- a) acceleratory
- b) constant
- c) - e) deceleratory
- f) sigmoidal



II. Solids: Determination of kinetic data (A and E_a)

- Isothermal model-fitting method (analogous to homogeneous reactions)
  - 1. Determination of k from

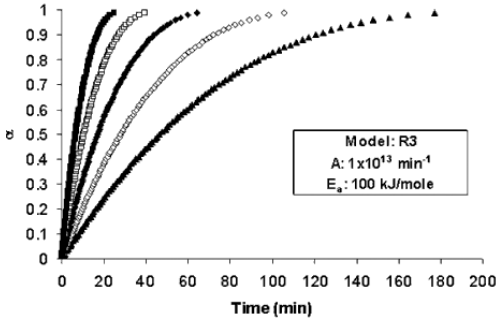
$$g(\alpha) = kt$$

by fitting the "best" model to the experimental data

  - 2. Determination of kinetic parameters using the Arrhenius equation

$$k = A \cdot e^{-\frac{E_a}{RT}}$$

a



b

α	Temperature (K)				
	340	345	350	355	360
	t (min)	t (min)	t (min)	t (min)	t (min)
0.01	0.75	0.45	0.27	0.17	0.11
0.02	1.51	0.91	0.55	0.34	0.21
.	.				.
.	.	Experiment			.
.	.	.	.	.	.
0.98	164.44	98.33	59.87	36.87	22.98
0.99	177.04	105.73	64.32	39.63	24.82

α	g(α)				
	A2	A3	……..	R2	R3
0.01	0.10	0.22	……..	0.00	0.00
0.02	0.14	0.27	……..	0.01	0.01
.	.			.	.
.	.	Model		.	.
.	.			.	.
0.98	1.98	1.58	……..	0.89	0.73
0.99	2.15	1.66	……..	0.90	0.78

fit: g(α) = kt

c

T = 340 K

α	A2		A3		……..	R2		R3	
	g(α)	t (min)	g(α)	t (min)	……..	g(α)	t (min)	g(α)	t (min)
0.01	0.10	0.75	0.22	0.75	……..	0.00	0.75	0.00	0.75
0.02	0.14	1.51	0.27	1.51	……..	0.01	1.51	0.01	1.51
.	.	.	.	.	……..	.	.	.	.
.	.	.	.	.	……..	.	.	.	.
.	.	.	.	.	……..	.	.	.	.
0.98	1.98	164.44	1.58	164.44	……..	0.89	164.44	0.73	164.44
0.99	2.15	177.04	1.66	177.04	……..	0.90	177.04	0.78	177.04
Intercept	0.2990		0.4889		……..	0.0285		0.0001	
Slope (k)	**0.0104**		**0.0072**		……..	**0.0054**		**0.0044**	
r	0.9933		0.9760		……..	0.9966		1.0000	

T = 360 K

α	A2		A3		……..	R2		R3	
	g(α)	t (min)	g(α)	t (min)	……..	g(α)	t (min)	g(α)	t (min)
0.01	0.10	0.11	0.22	0.11	……..	0.00	0.11	0.00	0.11
0.02	0.14	0.21	0.27	0.21	……..	0.01	0.21	0.01	0.21
.	.	.	.	.	……..	.	.	.	.
.	.	.	.	.	……..	.	.	.	.
.	.	.	.	.	……..	.	.	.	.
0.98	1.98	22.98	1.58	22.98	……..	0.89	22.98	0.73	22.98
0.99	2.15	24.82	1.66	24.82	……..	0.90	24.82	0.78	24.82
Intercept	0.2985		0.4885		……..	0.0282		-0.0001	
Slope (k)	**0.0745**		**0.0515**		……..	**0.0387**		**0.0317**	
r	0.9933		0.9761		……..	0.9967		1.0000	

d

Arrhenius fit

	A2		A3		……..	R2		R3	
	ln k	1/T	ln k	1/T	……..	ln k	1/T	ln k	1/T
	ln 0.0104	1/340	ln 0.0072	1/340	……..	ln 0.0054	1/340	ln 0.0044	1/340
	.		.	.	……..	.		.	.
	.	.	.	.	……..	.	.	.	.
	.	.	.	.	……..	.	.	.	.
	ln 0.0745	1/360	ln 0.0515	1/360	……..	ln 0.0387	1/360	ln 0.0317	1/360
Intercept (ln A)	30.81		30.44		……..	30.15		29.95	
Slope ($-E_a/R$)	-12025.75		-12026.09		……..	-12025.65		-12025.41	
r	-1.0000		-1.0000		……..	-1.0000		-1.0000	
A (min^{-1})	2.40×10^{13}		1.66×10^{13}		……..	1.25×10^{13}		1.02×10^{13}	
E_a (kJ/mol)	100.05		100.06		……..	100.05		100.05	

A. Khawam, D.R. Flanagan (2006)

II. Solids: Determination of kinetic data (A and E_a)

- Isothermal model-free fitting method (isoconversional, standard):

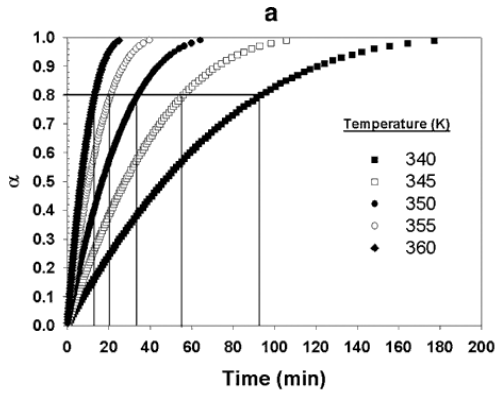
$$g(\alpha) = A \cdot e^{-\frac{E_a}{RT}} \cdot t$$

$$\ln g(\alpha) = \ln A - \frac{E_a}{RT} + \ln t$$

$$-\ln t = \ln \frac{A}{g(\alpha)} - \frac{E_a}{RT}$$

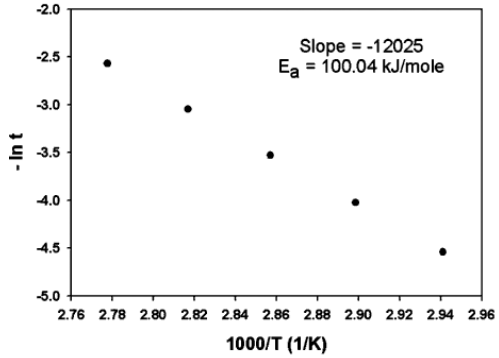
  - A plot of –ln t versus 1/T for each a gives E_a from the slope for that α regardless of the model

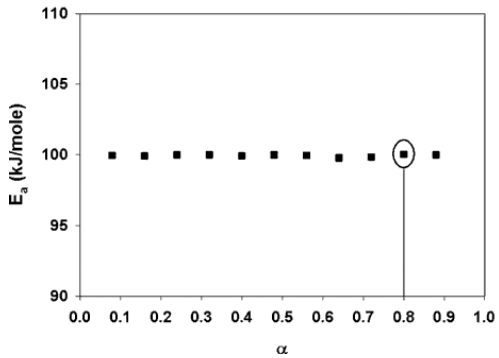
- Non-isothermal case
  - model-fitting: e.g. Freeman-Carroll method
  - model-free fitting: e.g. Kissinger
  - isoconversional: e.g. Ozawa-Flynn-Wall method



α = 0.80

Time (min)	94	56	34	21	13
Temp. (K)	340	345	350	355	360
- ln t	-4.54	-4.02	-3.53	-3.05	-2.57
10^3/T (K^{-1})	2.94	2.90	2.86	2.82	2.78





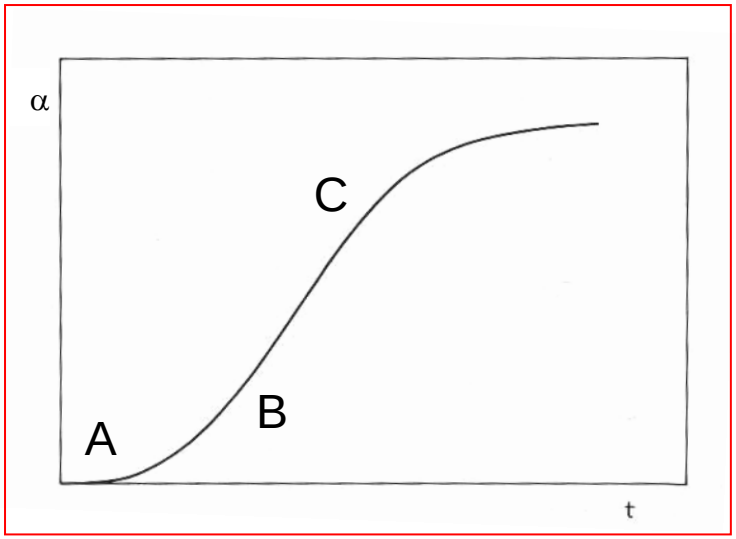
A. Khawam, D.R. Flanagan (2006)

III a. Decomposition reactions

A(s) → B(s) + C(g)

$CaCO_3$ → CaO + CO_2

- Typical isothermal α-t curve:
  - A: induction period
  - B: acceleration period
  - C: decay period



N.B. Hannay (ed) 1976

- Nucleation: Initiation of the reaction at specific reactive sites first at or near the crystal's surface (defects, dislocations)
  - Nucleus: Microcrystal that start crystallisation of a new phase
  - sensitive to pre-treatment (scratching, irradiation, …)

- Growth: Subsequent advancement of a reactive interface into the undecomposed bulk (Interface area ~ reaction rate)

- Reaction rate determined by number of nuclei present and the total area of the product/reactant interface

III a. Decomposition reactions

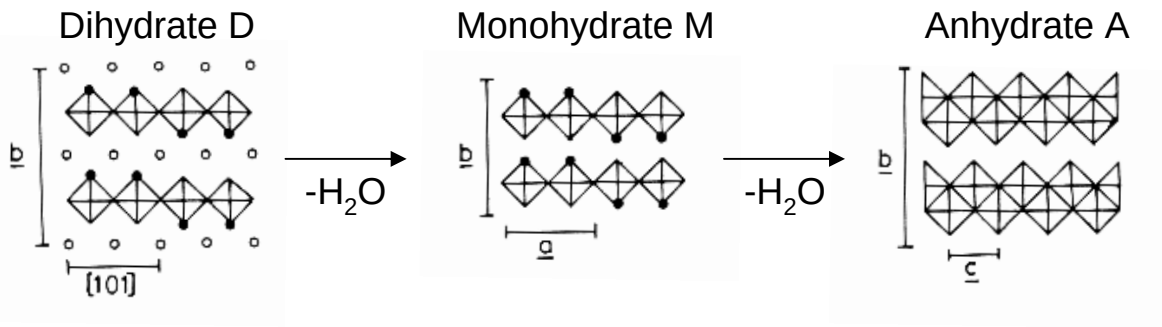
- Avrami-Erofe'ev: random nucleation, 3D growth

  $$kt = [-\ln(1-\alpha)]^{1/3} \qquad (A3)$$

- Prout-Tompkins: chain-branching mechanism

  $$kt = \ln[\alpha / (1-\alpha)] \qquad (B1)$$

- Topochemical decompositions: reaction controlled by crystal structure, atomic arrangement remains largely unaffected
  - Example: Dehydration of $MoO_3 \cdot 2\ H_2O$



Topotactic relations: $(010)_D||(010)_M$, $(010)_D||(010)_A$, …

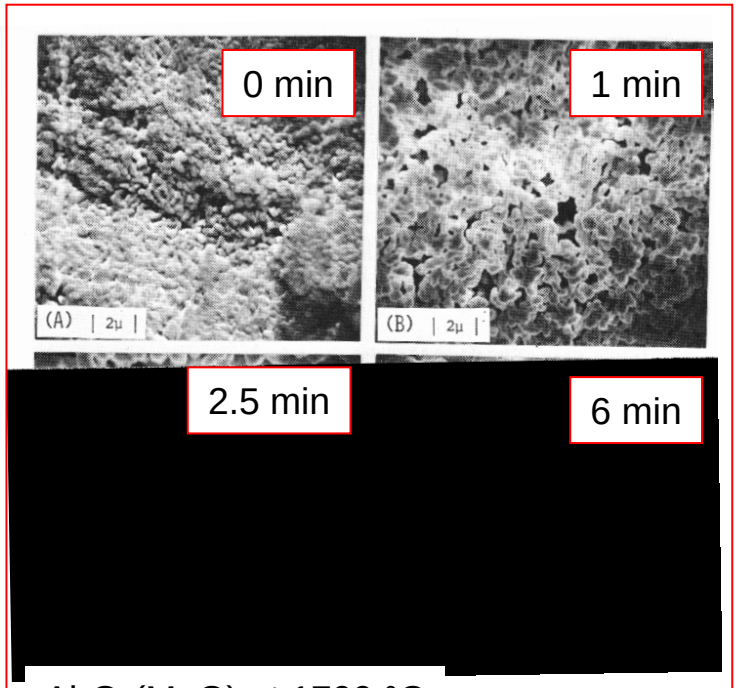
Mild thermal treatment of M → ReO_3-like MoO_3

C.N.R. Rao, J. Gopalakrishnan (1986)

III a. Sintering

- Joining of particles in a solid (0.5 - 0.75 T_M)
  - Reduction of surface free energy
  - Elimination of void volume (Shrinkage)

- Kuczynski: Neck growth between particles determined by diffusion of vacancies from the neck region to the grain boundary



Al_2O_3(MgO) at 1700 °C

N.B. Hannay (ed) 1976

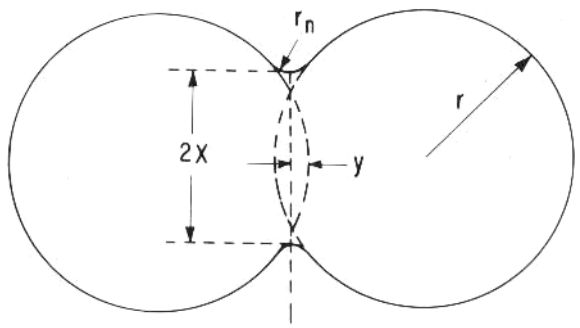


Fig. 2. Neck growth between spheres with mutual approach of centers. Shrinkage occurs.

$$\frac{dV}{dt} = D_v \cdot A \cdot \left(\frac{\Delta c}{r_n}\right) \cdot v$$

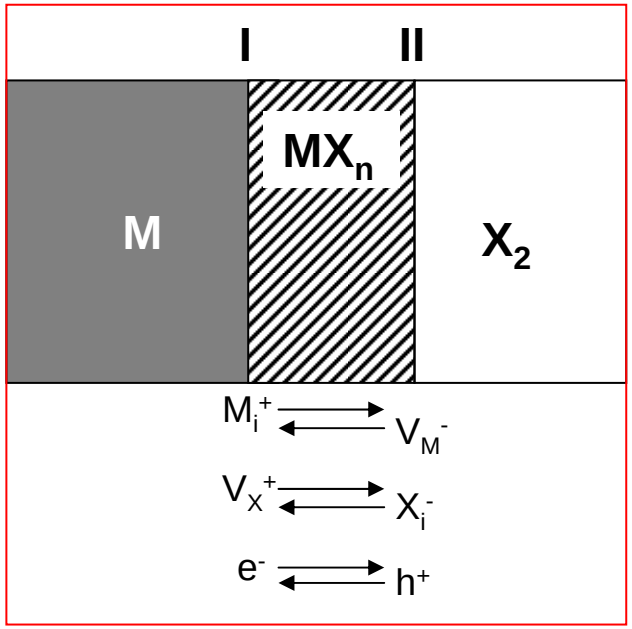
V: Neck volume
D_v: Diffusion coefficient for vacancies
A: neck area
Δc: concentration difference of vacancies in neck and bulk
r_n: Radius of neck
v: vacancy volume

III b. Solid-gas reactions

$M(s) + n/2\ X_2(g) \rightarrow MX_n(s)$

Oxidation of metals, tarnishing:

- Formation of a product layer at the s/g interface
- Porous layer: Linear rate law R1 (Pilling Bedworth criterion: $V_{m,MX} / V_{m,M} < 1$, e.g. oxidation of alkali metals)
- Compact layer: Transport of at least one reactant through the product
  - Oxidation of Cu to Cu_2O
    p-type semiconductor defect equilibrium
    $O_2(g) \rightleftarrows 2\ O + 4\ V_{Cu}^- + 4\ h^+$
    Rate-determining: II → I of V_{Cu}^-, h^+
  - Oxidation of Zn to ZnO
    n-type semiconductor defect equilibrium
    $ZnO \rightleftarrows Zn_i^+ + e^- + ½O_2(g)$
    Rate-determining: I → II of Zn_i^+, e^-



III b. Solid-gas reactions

- Tammann 1920: Parabolic growth kinetics of thick product layers (x>100nm)

$$\frac{dx}{dt} = \frac{k}{x} \qquad x^2 = k_p t + C$$

x: thickness of product layer

- Parabolic rate law is indicative of reactant diffusion being rate-limiting

- Wagner's model: Diffusion of reactants under the influence of the electrical force of the redox-reaction (quantitatively e.g in Skinner 1974)
  - diffusion of metal from I to II (e.g. oxidation of Co)
  - diffusion of oxygen from II to I (e.g. oxidation of Ti)
  - driving force: $\Delta G = -n F E < 1$; E is the voltage across the oxide layer
  - determined by the defect structure of the metal oxide
  - transported species are ions and electrons/holes instead of neutral atoms

III b. Solid-gas reactions

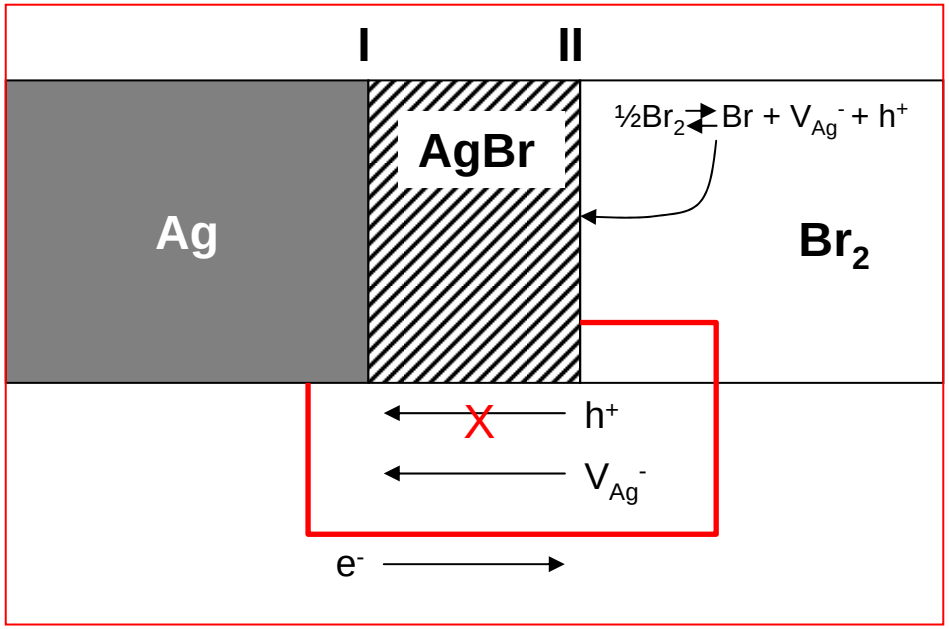
- Application of Wagner's model: Bromination of Ag

  $Ag(s) + ½ Br_2(g) \rightarrow AgBr(s)$

- Experiment:
  - Parabolic rate law
  - $k \sim p(Br_2)^{1/2}$

- Reaction rate decreases as Ag is alloyed with small quantities of Zn or other divalent species

- Reaction rate increases as Ag and AgBr are short-circuited with a Pt wire

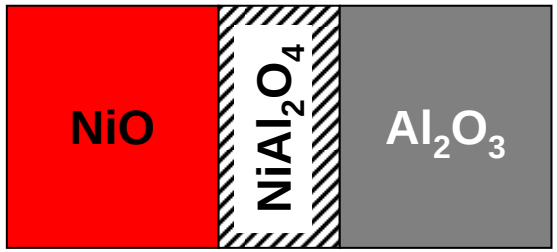


III c. Solid-solid reactions

$m\,A(s) + n\,B(s) \rightarrow A_mB_n(s)$ Addition reaction

$NiO + Al_2O_3 \rightarrow NiAl_2O_4$ Spinel formation

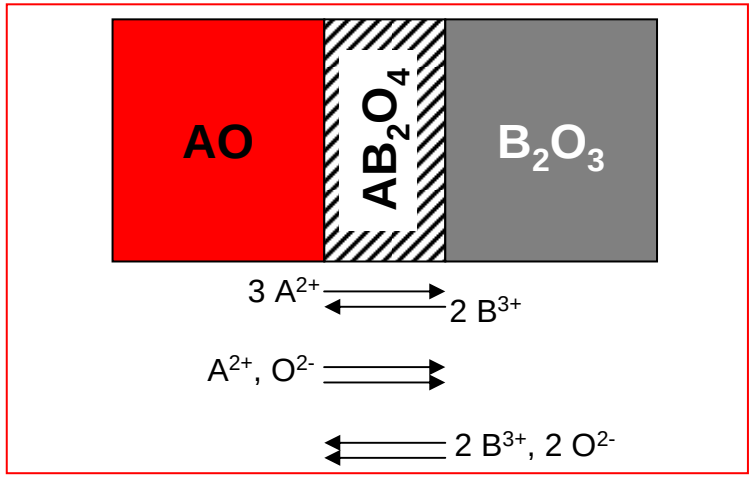
- A product layer spatially separates the reactants, subsequent reaction requires mass transport through the product layer

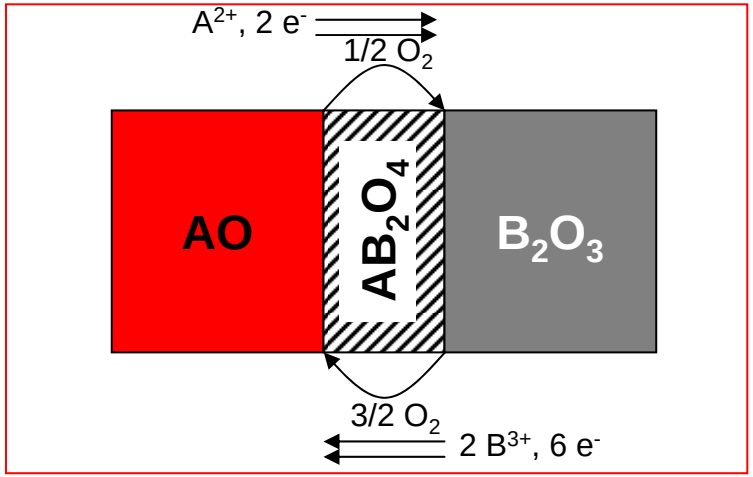


- Theoretical treatment of solid-solid reaction based on defect thermodynamics and phenomenological diffusion theory (Schmalzried 1995)
- Spinel growth generally follows a parabolic rate law (for x > 1µm), diffusion-limited

III c. Solid-solid reactions

- Wagner mechanism: Counter flux of cations/electrons maintaining electrical neutrality

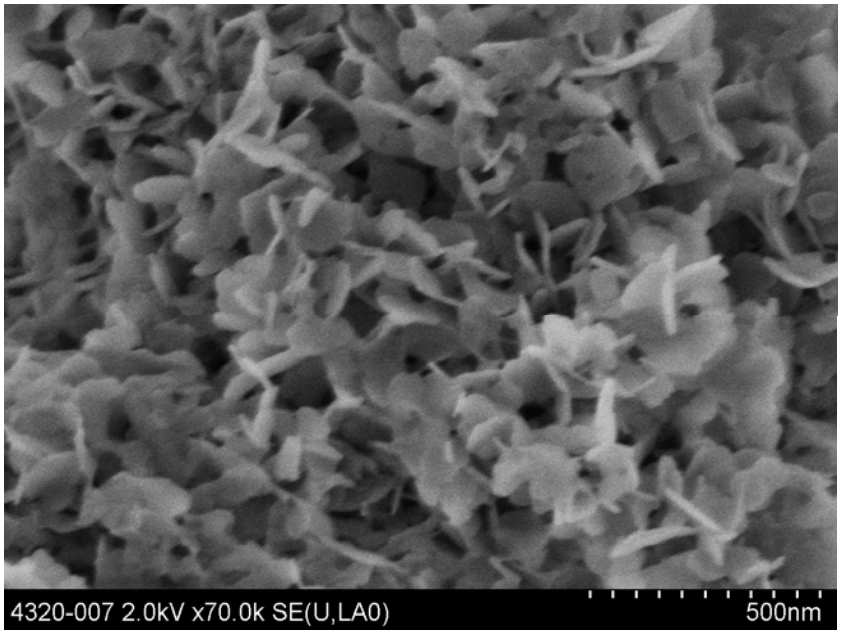




- Sometimes additional oxygen transport through the gas phase observed (Redox-chemistry of transition metal required)
- Reaction of MgO (NaCl-type) and Cr_2O_3 single crystals yields monocrystalline spinel (rearrangement of metal cations in essentially unchanged ccp oxygen lattice)
- but: polycrystalline NiO and α-Al_2O_3 single crystals also yield monocrystalline spinel (change of oxygen packing hcp → ccp followed by cation redistribution)

III c. Solid-solid reactions

- Kinetics of solid-solid reactions are much more complicated if
  - reactants are polycrystalline
  - reactant/product geometry is ill-defined
  - products are partially soluble
  - more than one product are formed (e.g. exchange reactions $ZnS + CdO \rightarrow ZnO + CdS$)

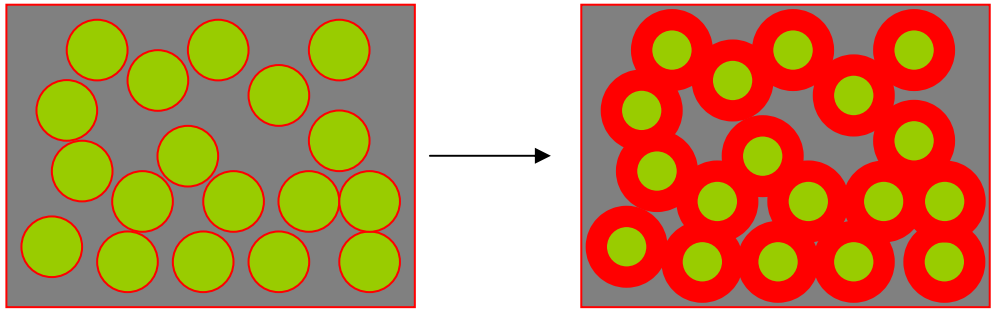


- Parameters: Particle size, size distribution, packing density, contact areas, porosity, …
  (generally the importance of these parameters increases with decreasing reaction temperature)

III c. Solid-solid reactions

- Jander's model for powder reactions (D3)

- Assumptions:
  - Spheres of **A** (all of the same size) are embedded in a quasicontinuous medium **B**
  - the thickness of the **reaction product** follows a parabolic rate law



$$g(\alpha) = [1-(1-\alpha)^{\frac{1}{3}}]^2 = \frac{2k_p t}{r_A^2}$$

k_p: Practical parabolic rate constant
r_A: Radius of A particles

- Assumptions are clearly oversimplified. However, parabolic rate laws are often observed

- Kinetics of the powder reaction

$ZnO + Al_2O_3 \rightarrow ZnAl_2O_4$ (closed system at 1400 °C)

can be described by Carter's equation (based on Jander's equation corrected for different molar volumes of reactant and product, but: ZnO in the gas phase)

III d. Solid-liquid reactions

- Simplest case: Dissolution of a solid in a liquid

$$\frac{dc}{dt} = k \cdot S \cdot (c_{sa} - c)$$

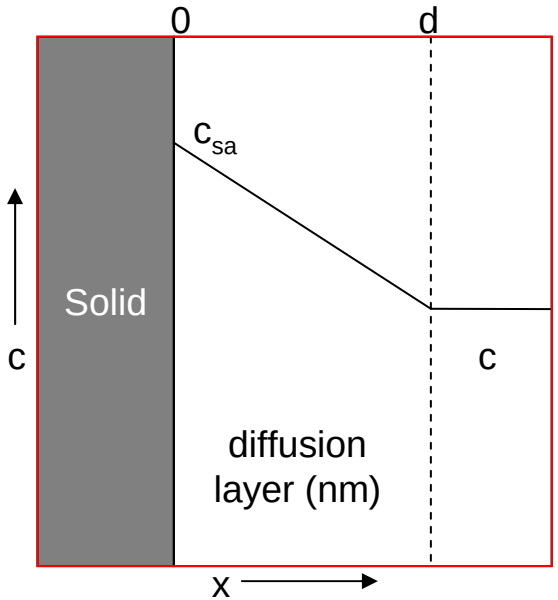
S: Surface area of solid
c_{sa}: saturation concentration

Fick's 1st law: $$j = \frac{1}{S}\frac{dn}{dt} = -D\frac{dc}{dx}$$

$$\frac{dc}{dx} = -\frac{c_{sa} - c}{d}$$

$$\frac{dc}{dt} = S\frac{D}{d \cdot V}(c_{sa} - c)$$

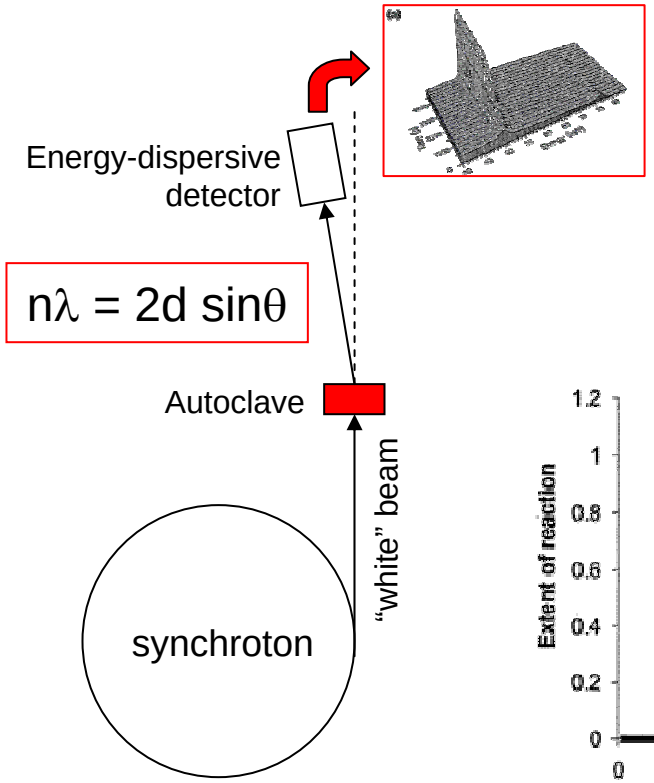
$$\boxed{k = \frac{D}{d \cdot V}}$$

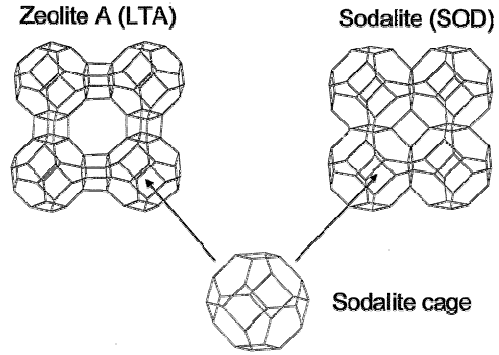


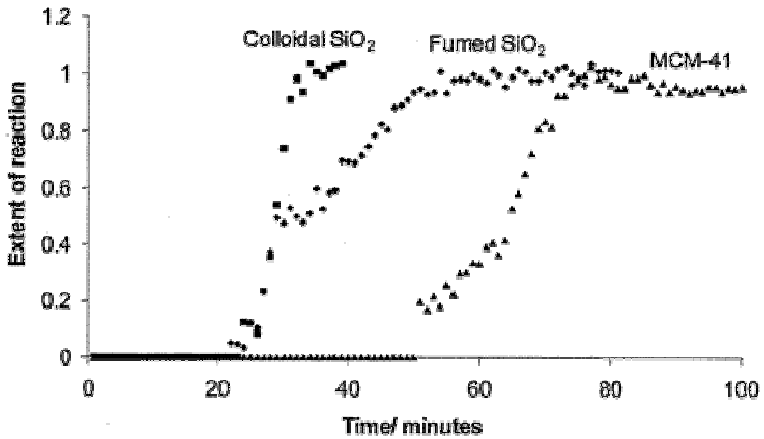
- Temperature dependence of k and D equal for many dissolution processes: Dissolution is diffusion controlled (e.g. salt in water, Mg in HCl)
- Chemical control observed for other systems (Al in HCl, Cu in HNO_3) due to e.g. redox-chemistry, passivation, complex formation
- Influence of crystallographic plane exposed, particle size, surface defects (etch pit formation), …
- Corrosion and electrodeposition – typical textbook examples discussed e.g. in Hannay (ed.) 1976
- Precipitation: Nucleaction and crystal growth depend on supersaturation

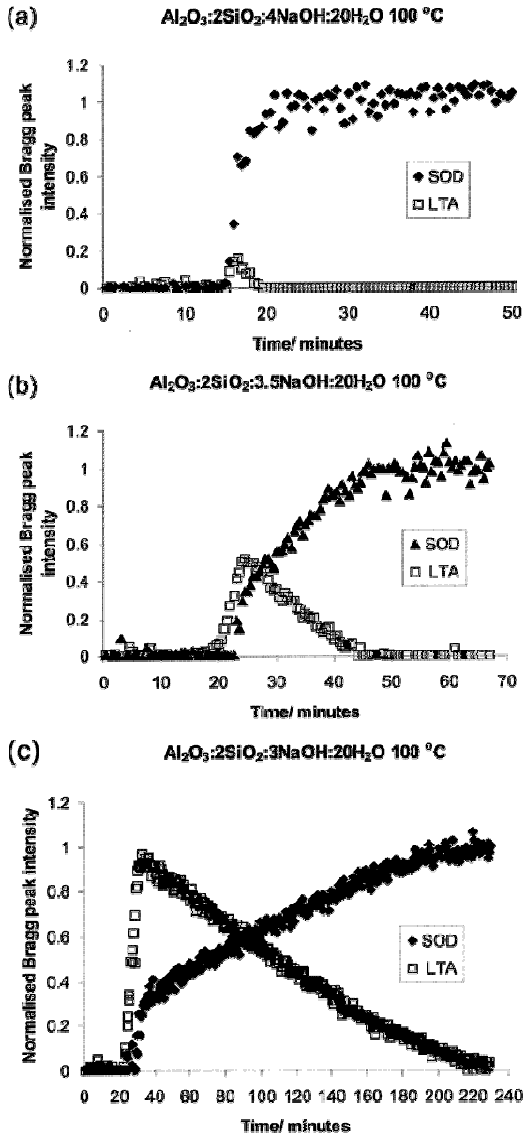
IV. Examples: Hydrothermal Synthesis

- Hydrothermal synthesis of zeolite A investigated by energy-dispersive X-ray diffraction (EDXRD)





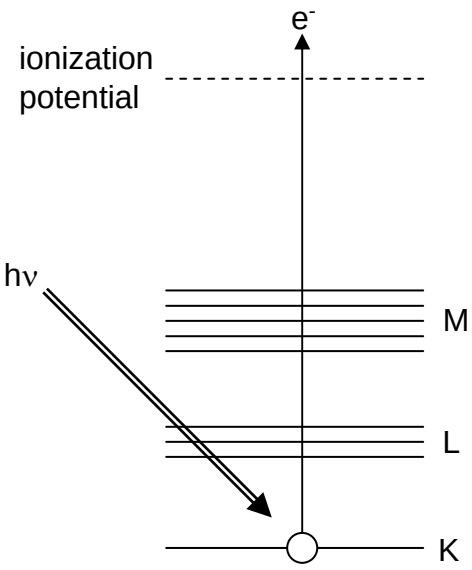


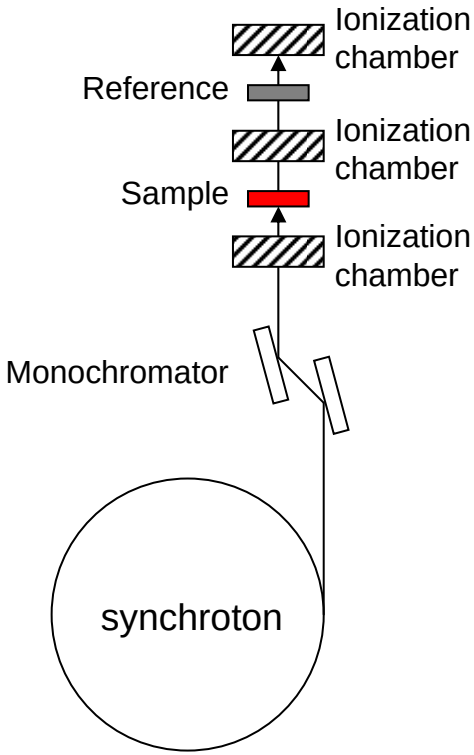


R.I. Walton, F. Millange, D. O'Hare, A.T Davies, G. Sankar, C. Richards, A. Catlow, J. Phys. Chem. B 105 (2007) 83-90.

IV. Examples: Reduction

- Activation of a Cu catalyst studies with in-situ X-ray absorption spectroscopy (XAS)
- XANES: X-ray absorption near edge structure





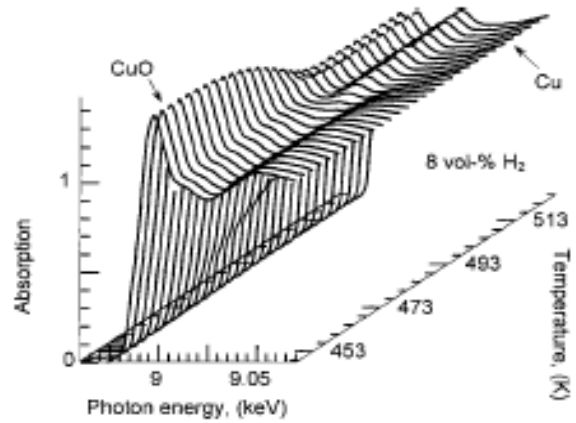


Figure 1. Evolution of Cu K edge XANES spectra of a CuO/ZnO sample (70 at% Cu, 30 at% Zn) during temperature-programmed reduction in 8 vol% H_2 with a heating rate of 5 K/min [29]. The characteristic near-edge features of the two majority phases CuO and Cu are indicated.

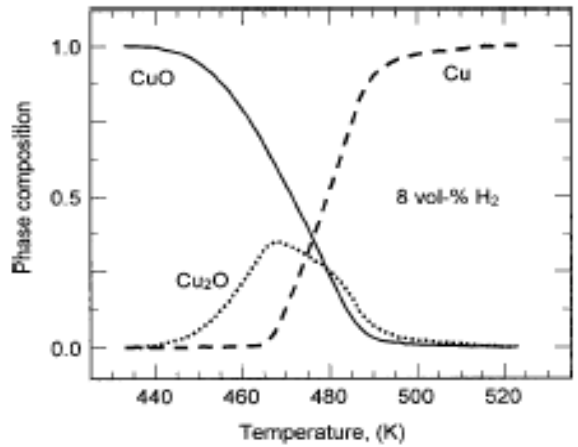


Figure 2. Phase composition during temperature-programmed reduction of a CuO/ZnO sample (70 at% Cu, 30 at% Zn) in 8 vol% H_2 with a heating rate of 5 K/min [29].

T. Ressler, J. Wienold, R.E. Jentoft, T. Neisius, M.M. Günter, Topics in Catalysis 18 (2002) 45.

V. Summary: Kinetics of solids

- Kinetics of solids: Methods of homogeneous kinetics do not apply
  - transport phenomena are involved in reactions of solids
    - Mass transport is closely related to the defect structure of the solid reactant
    - Increase of reaction temperature favours diffusion, but also thermodynamics
  - the reactions zone is confined
- Several models available for $g(\alpha)$ basing on different assumptions concerning the reaction type and mechanism
- Methods available to extract kinetic data ($g(\alpha)$, A, E_a) from isothermal and non-isothermal measurements
  - model- and model-free fitting (e.g. isoconversional)
- Thermal analysis (TGA, DTA, DSC) and Temperature-programmed reactions (TPR, TPO)
  - accurate for $\alpha(t)$, $\alpha(T)$, but not specific
- Time-resolved Diffraction (XRD, EDXRD) and spectroscopy (XAS, Raman, IR, …)
  - less accurate for $\alpha(t)$, $\alpha(T)$, but specific
  - additional chemical or structural information

VI. Critical review

- What is the goal of my kinetic study?
  - For solid state preparation: determination and comparison of stabilities of intermediates and product, revealing solid state reaction mechanisms

- "… the unfortunate fact is that, since, in thermal analysis, properties of a system are measured as a function of time and temperature, all thermoanalytical results are potentially kinetic data, and many people ill grounded on kinetics feel obliged to perform a "kinetical analysis" of them …"

  (J.J. Flynn, Chairman of the Kinetics Subcommittee of the International Confederation for Thermal Analysis, quoted in M. Maciejewski, J. Thermal Anal. 33 (1988) 1269)

- What can I conclude from kinetic data of a solid state reaction?

- Problems are related to
  - physical meaning of kinetic parameters
  - correlation between real chemical phenomena and kinetic models
  - reproducibility (influence of experimental conditions)

VI. Critical review

- $CaCO_3 \rightarrow CaO + CO_2$
  - Reaction is influenced by
    - sintering before decomposition
    - pressure of CO_2 during decomposition
    - simultaneous polymorphic transition
  - Models do not account for these phenomena

- Solid state reactions are complex: Models often are oversimplified or unrealistic (e.g. F1: only one nucleation site per particle)

- Care must be taken in deducing solid state reaction mechanisms solely from kinetic data without complementary (chemically or structurally sensitive) techniques (weight change is not enough)
  - Do not conclude the particle shape from the Avrami-exponent of a TG fit alone, use a microscope!
  - Avoid "$CaCO_3$ decomposes according to a nuceation-growth mechanism.", rather state: "The decompostion of our sample of $CaCO_3$ under the given experimental conditions can be best described by a model assuming a nucleation-growth mechanism."

VI. Critical review

- Physical meaning of activation energies in solid state reactions
  - Solid state kinetics are completely described by $g(\alpha)$, A and E_a (kinetic triple), in a strict sense activation energies can only be compared if the other two parameters are coincidently equal
  - E_a has been observed to vary with α in solid state reactions (change of reactivity, complex mechanism)
  - E_a of isothermal and non-isothermal experiments are usually not in agreement for solid state reactions

- If carefully used and complemented with other techniques the analysis of solid state kinetics can give indications on the reaction mechanism and yields valuable information on the reactivity that can be very helpful for the development of preparative strategies

Literature

- C.N.R. Rao, J. Gopalakrishnan: New directions in solid state chemistry, Cambridge University Press (1986)

- N.B. Hannay (ed.): Treatise on solid state chemistry, Plenum Press, New York (1976)
  - A.D. LeClaire: Diffusion, p.1
  - F.C. Tompkins: Decomposition Reactions, p.193
  - H. Schmalzried: Solid State Reactions, p.233
  - J.E. Burke, J.H. Rosolowski: Sintering, p.621

- G.B. Skinner: Introduction to chemical kinetics, Academic Press, New York (1974)

- H. Schmalzried: Chemical kinetics of solids, VCH, Weinheim (1995)

- S.E. Dann: Reactions and characterization of solids, RSC, Cambridge (2000)

- K. Schwetlick, H. Dunken, G. Pretzschner, K. Scherzer, H.-J. Tiller: Chemische Kinetik, Verlag Chemie, Weinheim (1972)

- L. Smart, E. Moore: Einführung in die Festkörperchemie, Vieweg, Braunschweig (1997)

- A. Khawam, D.R. Flanagan: Basics and Applications of Solid State Kinetics: A Pharmaceutical Perspective, Journal of Pharmaceutical Sciences 95 (2006) 472.