

# Comparing Mechanistic and Thermochemical Modelling of Reaction Rate-Controlled Multiphase Systems

## Simulation of the Titanium(IV)Chloride Oxidizer

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# **CONTENTS OF PRESENTATION**

- 1. Motivation to calculate rate-controlled systems**
- 2. Coupling of reaction matrix with stoichiometric formula matrix**
- 3. Case example:  $\text{TiO}_2$  nanoparticle formation by  $\text{TiCl}_4$  oxidation**
  - detailed kinetic mechanism (DKM, West & al. 2007-2009)
  - constrained Gibbs energy (CFE, by Koukkari & al. 1993  $\Rightarrow$ )
  - comparison with experiment
- 4. Application in reactor simulation**
- 5. Conclusions**



# MOTIVATION

- Practical systems seldom reach complete equilibrium due to (slow) reaction kinetics
- The reaction rate parameters of many suggested complex mechanisms are often less well known
- mechanistic (DKM) modeling is a nearly impossible challenge for complex heterogeneous systems with many phases
  
- ⇒ it would be advantageous to include reaction rate restrictions to Gibbs energy minimization to allow for calculations of kinetically constrained reactors

# MODELLING OF DYNAMIC MULTICOMPONENT SYSTEMS

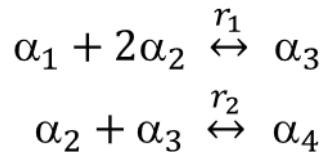
- Solve time course for amount of moles vs. extents of reaction ( $\xi$ ):

$$d\mathbf{n} = \mathbf{v} d\xi \quad ; \quad \xi = \xi(t)$$

- In DKM, a group of ODE's used and solved as a numerical initial value problem; parameters for all reaction rates required (e.g. CANTERA)
- when solving  $\min(G)$  for global minimum, the  $\xi$ 's are independent variables, but components are conserved by mass balance constraints
- In constrained  $\min(G)$  [CFE] the  $\xi = \xi(t)$  are solved from reaction rate equations to be used as additional conserved quantities
- ⇒ in CFE differential-algebraic (DA) approach is used, rate parameters applied for selected reactions only and a ‘timewise’ sequential  $\min(G)$  is calculated (e.g. ChemSheet/ChemApp)

# COUPLING OF REACTION AND CONSERVATION MATRICES

Example of 2 reactions:



Constraints in the 2-component system:

- ✓ **2 components**  $(\alpha_1, \alpha_2)$
- ✓ **4 species**  $(\alpha_1, \alpha_2, \alpha_3, \alpha_4)$
- ✓ **2 reactions**  $(r_1, r_2)$

Reaction matrix

$$v = \begin{array}{c|cc} & r_1 & r_2 \\ \hline -1 & 0 & \alpha_1 \\ -2 & -1 & \alpha_2 \\ 1 & -1 & \alpha_3 \\ 0 & 1 & \alpha_4 \end{array}$$

Stoichiometric formula matrix

$$\Leftrightarrow C^T = \left[ \begin{array}{cc|c} 1 & 0 & \alpha_1 \\ 0 & 1 & \alpha_2 \\ 1 & 2 & \alpha_3 \\ 1 & 3 & \alpha_4 \end{array} \right]$$

Formula matrix with reaction constraints

Use row permutations<sup>(\*)</sup>  
in  $[I, v]$  to convert  $v$   
as constraints in  $C$ :

$\Rightarrow \Rightarrow \Rightarrow \Rightarrow \Rightarrow$

$$C(v)^T = \left[ \begin{array}{cccc|c} 1 & 0 & -1 & 0 & \alpha_1 \\ 0 & 1 & 0 & 0 & \alpha_2 \\ 1 & 2 & 0 & 0 & \alpha_3 \\ 1 & 3 & 0 & 1 & \alpha_4 \\ 0 & 0 & 1 & 0 & r_1 \\ 0 & 0 & 0 & 1 & r_2 \end{array} \right]$$

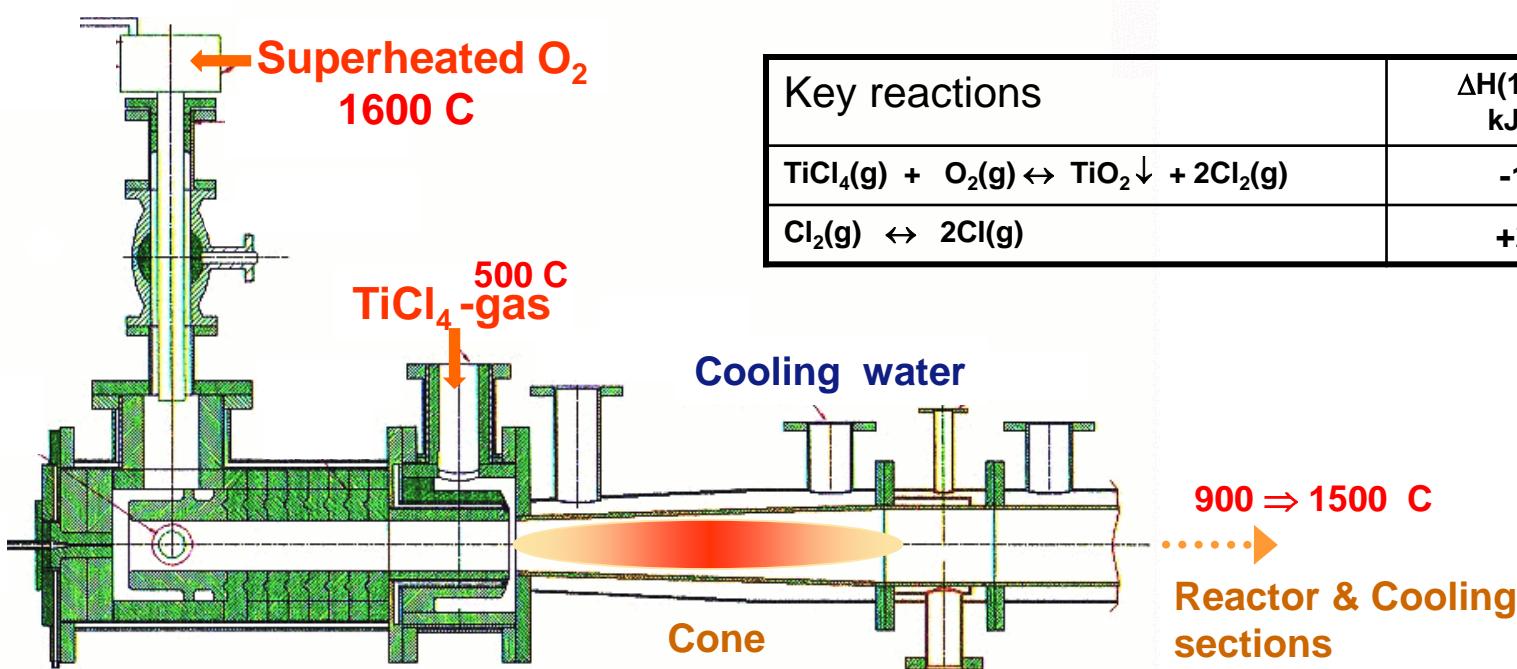
- $\Rightarrow C(v)$
- ✓ includes constraints for mass balances and reactions
  - ✓ applies extents of reaction as additional constraints in  $\min(G)$
  - ✓ number of constrained reactions can be chosen ( $0 \leq r \leq R$ )

<sup>(\*)</sup> Blomberg & Koukkari, Comput. Chem. Eng. 35 (2011) 1238-1251.

Pajarre & al., Chem. Eng.Sci. 146 (2016) 244-258.

Koukkari & Paiva, Chem.Eng.Sci 179 (2018), 227-242.

# EXAMPLE: FLAME REACTOR FOR $\text{TiCl}_4$ OXIDATION



- $\text{TiO}_2$  is formed as a nanoparticle suspension – used as the white pigment (> 5 Mt/yr)
- exothermic main reaction compensated by endothermic side reactions (chlorine dissociation,  $\text{Ti}_x\text{O}_y\text{Cl}_z$  formation) and efficient reactor cooling

# SYSTEM FOR DKM CALCULATIONS ( $\text{TiCl}_4$ OXIDATION)

## WEST 2007

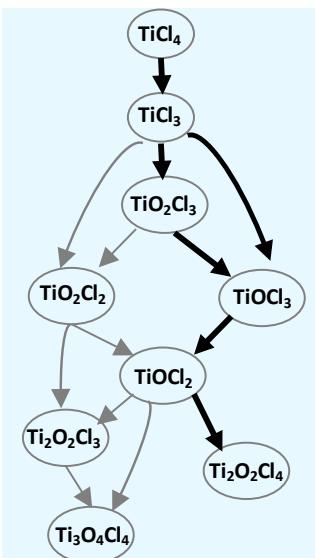
### System

O  
 $\text{O}_2$   
 $\text{O}_3$   
 Cl  
 $\text{Cl}_2$  Gas  
 ClO  
 ClOO  
 $\text{Cl}_2\text{O}$   
 Ti  
 $\text{TiCl}$   
 $\text{TiCl}_2$   
 $\text{TiCl}_3$   
 $\text{TiCl}_4$   
 $\text{TiOCl}_2$   
 $\text{TiOCl}_3$   
 $\text{TiO}_2\text{Cl}_2$   
 $\text{TiO}_2\text{Cl}_3$   
 $\text{TiCl}_2\text{OCl}$   
 $\text{Ti}_2\text{O}_2\text{Cl}_3$   
 $\text{Ti}_2\text{O}_2\text{Cl}_4$   
 $\text{Ti}_2\text{O}_2\text{Cl}_5$   
 $\text{Ti}_2\text{O}_2\text{Cl}_6$   
 $\text{Ti}_2\text{O}_3\text{Cl}_2$   
 $\text{Ti}_2\text{O}_3\text{Cl}_3$   
 $\text{Ti}_3\text{O}_4\text{Cl}_4$   
 $\text{TiO}_2\text{Cl}_5$   
 $\text{TiO}_2\text{Cl}_6$   
 $\cdot$   
 $\text{TiO}_2(\text{s})$  Solid

### Overall reaction



### Reaction mechanism



Richard H. West  
 A dissertation submitted for the degree of  
 Doctor of Philosophy at the



UNIVERSITY OF  
 CAMBRIDGE

2007

Table 6.2: Reaction mechanism equations.

No	Reaction	$\Delta H^\circ_{298K}{}^a$	$A{}^b$	$n$	$E_a{}^c$	Ref.
<b>Thermal Decomposition</b>						
R1	$\text{TiCl}_4 + \text{M} \rightleftharpoons \text{TiCl}_3 + \text{Cl} + \text{M}$	387	$5.40 \times 10^{18}$	0	336	10
R2	$\text{TiCl}_3 + \text{M} \rightleftharpoons \text{TiCl}_2 + \text{Cl} + \text{M}$	422	$7.70 \times 10^{18}$	0	387	10
R3	$\text{TiCl}_2 + \text{M} \rightleftharpoons \text{TiCl} + \text{Cl} + \text{M}$	507	$3.20 \times 10^{17}$	0	511	11
R4	$\text{Ti} + \text{Cl} \rightleftharpoons \text{TiCl}$	-405	$1.00 \times 10^{13}$	0	0	
R5	$\text{TiCl}_2 + \text{Cl}_2 \rightleftharpoons \text{TiCl}_4$	-567	$1.00 \times 10^{13}$	0	0	
R6	$\text{TiCl} + \text{Cl}_2 \rightleftharpoons \text{TiCl}_3$	-687	$1.00 \times 10^{13}$	0	0	
<b>Abstraction and Disproportionation</b>						
R7	$\text{TiCl}_3 + \text{Cl}_2 \rightleftharpoons \text{TiCl}_4 + \text{Cl}$	-144	$1.00 \times 10^{13}$	0	0	
R8	$\text{TiCl}_2 + \text{Cl}_2 \rightleftharpoons \text{TiCl}_3 + \text{Cl}$	-180	$1.00 \times 10^{13}$	0	0	
R9	$\text{TiCl} + \text{Cl}_2 \rightleftharpoons \text{TiCl}_2 + \text{Cl}$	-265	$1.00 \times 10^{13}$	0	0	
R10	$\text{Ti} + \text{Cl}_2 \rightleftharpoons \text{TiCl} + \text{Cl}$	-162	$1.00 \times 10^{13}$	0	0	
R11	$\text{TiCl}_4 + \text{TiCl} \rightleftharpoons \text{TiCl}_3 + \text{TiCl}_2$	-121	$1.00 \times 10^{13}$	0	0	
R12	$\text{TiCl}_4 + \text{Ti} \rightleftharpoons \text{TiCl}_3 + \text{TiCl}$	-18	$1.00 \times 10^{13}$	0	0	
R13	$\text{TiCl}_2 + \text{TiCl} \rightleftharpoons \text{TiCl}_3 + \text{Ti}$	-17	$1.00 \times 10^{13}$	0	0	
R14	$2 \text{TiCl} \rightleftharpoons \text{TiCl}_2 + \text{Ti}$	-103	$1.00 \times 10^{13}$	0	0	
R15	$\text{Cl}_2 + \text{Ti}_2\text{O}_2\text{Cl}_2 \rightleftharpoons \text{Cl} + \text{Ti}_2\text{O}_2\text{Cl}_3$	-95	$1.00 \times 10^{13}$	0	0	
R16	$\text{Cl}_2 + \text{Ti}_2\text{O}_2\text{Cl}_3 \rightleftharpoons \text{Cl} + \text{Ti}_2\text{O}_2\text{Cl}_4$	-174	$1.00 \times 10^{13}$	0	0	
R17	$2 \text{TiCl}_3 \rightleftharpoons \text{TiCl}_2 + \text{TiCl}_4$	35	$9.60 \times 10^{12}$	0	35	10 d
R18	$\text{TiCl}_3 + \text{TiCl} \rightleftharpoons 2 \text{TiCl}_2$	-85	$1.00 \times 10^{13}$	0	0	
<b>Oxidation</b>						
R19	$\text{TiCl}_3 + \text{O}_2 \rightleftharpoons \text{Ti}_2\text{O}_2\text{Cl}_3$	-277	$1.00 \times 10^{13}$	0	0	
R20	$\text{TiOCl}_3 + \text{ClO} \rightleftharpoons \text{Ti}_2\text{O}_2\text{Cl}_3 + \text{Cl}$	-115	$1.00 \times 10^{13}$	0	0	
R21	$\text{Ti}_2\text{O}_2\text{Cl}_3 + \text{TiCl}_3 \rightleftharpoons 2 \text{TiOCl}_3$	-7	$1.00 \times 10^{13}$	0	0	
R22	$\text{TiOCl}_2 + \text{Cl} \rightleftharpoons \text{TiOCl}_3$	-162	$1.00 \times 10^{13}$	0	0	
R23	$\text{TiOCl}_3 + \text{O} \rightleftharpoons \text{Ti}_2\text{O}_2\text{Cl}_3$	-384	$1.00 \times 10^{13}$	0	0	
R24	$\text{Ti}_2\text{O}_2\text{Cl}_2 + \text{Cl} \rightleftharpoons \text{TiOCl}_3$	-337	$1.00 \times 10^{13}$	0	0	
R25	$\text{Ti}_2\text{O}_2\text{Cl}_2 + \text{Cl} \rightleftharpoons \text{TiCl}_3 + \text{O}_2$	-61	$1.00 \times 10^{13}$	0	0	
R26	$\text{TiOCl}_3 + \text{O} \rightleftharpoons \text{TiCl}_3 + \text{O}_2$	-108	$1.00 \times 10^{13}$	0	0	
R27	$\text{TiCl}_2 + \text{O}_2 \rightleftharpoons \text{TiOCl}_2 + \text{O}$	-152	$1.00 \times 10^{13}$	0	0	
R28	$\text{Ti}_2\text{O}_2\text{Cl}_2 + \text{O} \rightleftharpoons \text{TiOCl}_2 + \text{O}_2$	-289	$1.00 \times 10^{13}$	0	0	
R29	$\text{TiCl}_3 + \text{ClO} \rightleftharpoons \text{TiCl}_4 + \text{O}$	-118	$1.00 \times 10^{13}$	0	0	
R30	$\text{TiCl}_2 + \text{ClO} \rightleftharpoons \text{TiCl}_3 + \text{O}$	-153	$1.00 \times 10^{13}$	0	0	
R31	$\text{TiCl} + \text{ClO} \rightleftharpoons \text{TiCl}_2 + \text{O}$	-239	$1.00 \times 10^{13}$	0	0	
R32	$\text{Ti} + \text{ClO} \rightleftharpoons \text{TiCl} + \text{O}$	-136	$1.00 \times 10^{13}$	0	0	
R33	$\text{TiCl}_3 + \text{O} \rightleftharpoons \text{TiOCl}_2 + \text{Cl}$	-228	$1.00 \times 10^{13}$	0	0	
R34	$\text{TiCl}_3 + \text{Cl}_2 \rightleftharpoons \text{TiCl}_4 + \text{ClO}$	-243	$1.00 \times 10^{13}$	0	0	
R35	$\text{TiCl}_3 + \text{ClO} \rightleftharpoons \text{TiOCl}_3 + \text{Cl}$	-122	$1.00 \times 10^{13}$	0	0	
R36	$\text{TiO}_2\text{Cl}_2 + \text{Cl} \rightleftharpoons \text{TiOCl}_2 + \text{ClO}$	-60	$1.00 \times 10^{13}$	0	0	

a

b

c

d

51...67 reactions

# DKM VS CONSTRAINED FREE ENERGY (CFE) APPROACH

## Mechanistic (DKM) model:

- 6 thermal decomposition reactions,  $\Delta H > 0$
- 12 abstractions and disproportionations,  $\Delta H < 0$
- 18 oxidation reactions,  $\Delta H < 0$
- 8 Cl/O-chemistry reactions,  $\Delta H >< 0$
- 7 dimerisation & dimer reactions  $\Delta H < 0$
  
- altogether 51 (67) reactions with estimated reaction rate data\*
  
- 23-28 ODE's with time as independent variable

## Thermodynamic (CFE) model:

- uses the reaction rate measured for the  $TiCl_4$ -conversion\*\*

$$\frac{d[TiCl_4]}{dt} = -k[TiCl_4] ; k = A \exp\left[\frac{-E_a}{RT}\right]$$

$$E_a = 73 \pm 2.8 \text{ kJ mol}^{-1} \quad (TiCl_4 : O_2 \sim 1:1) \quad \xi_r(t) = 1 - \frac{n(TiCl_4)}{n_0(TiCl_4)}$$

- apply  $\xi_r(t)$  as a constraint in Gibbs energy minimisation for  $TiCl_4$  consumption:

$$C(v) = \begin{bmatrix} O_2 & TiCl_4 & TiCl_3 & TiOCl_2 & \dots & Cl_2 & Cl & ClO & TiO_2 & r \\ 2 & 0 & 0 & 1 & \dots & 0 & 0 & 1 & 2 & 0 \\ 0 & 4 & 3 & 2 & \dots & 2 & 1 & 1 & 0 & 0 \\ 0 & 1 & 1 & 1 & \dots & 0 & 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 & \dots & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{matrix} O \\ Cl \\ Ti \\ c \end{matrix}$$

- assume all side reactions fast (LCE)

\*West & al., Ind. Eng. Chem. Res. 46, (2007) 6147.

Karlemo & al., Plasma Chem. & Plasma Proc. 16, (1996) 59.

\*\*Pratsinis & al., J. Am. Ceram. Soc., 70 (1990) 2158.

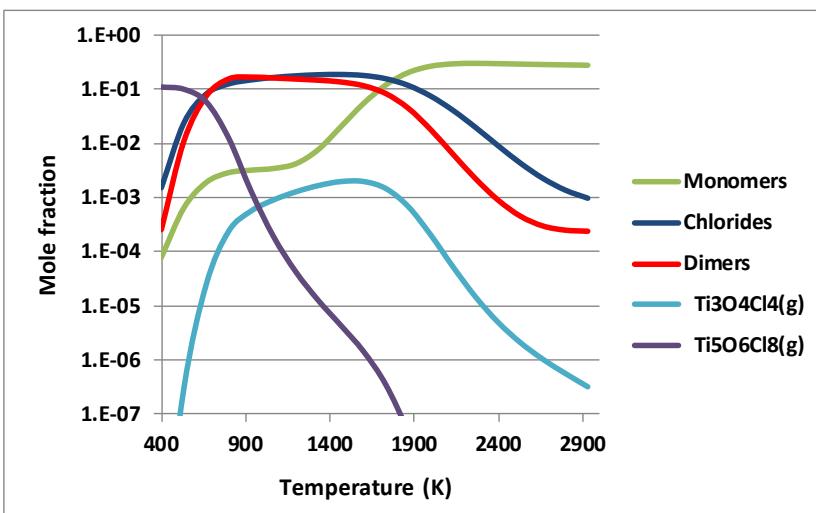
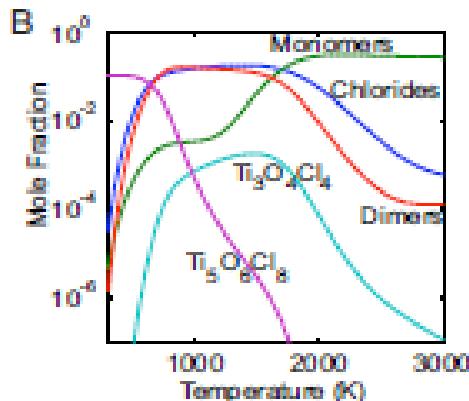
Koukkari & Liukkonen, Ind. Eng. Chem. Res., 41 (2002) 2931.

# COMPARISON OF THERMODYNAMIC DATA

GLOBAL EQUILIBRIUM [MIN(G) CALCULATION];

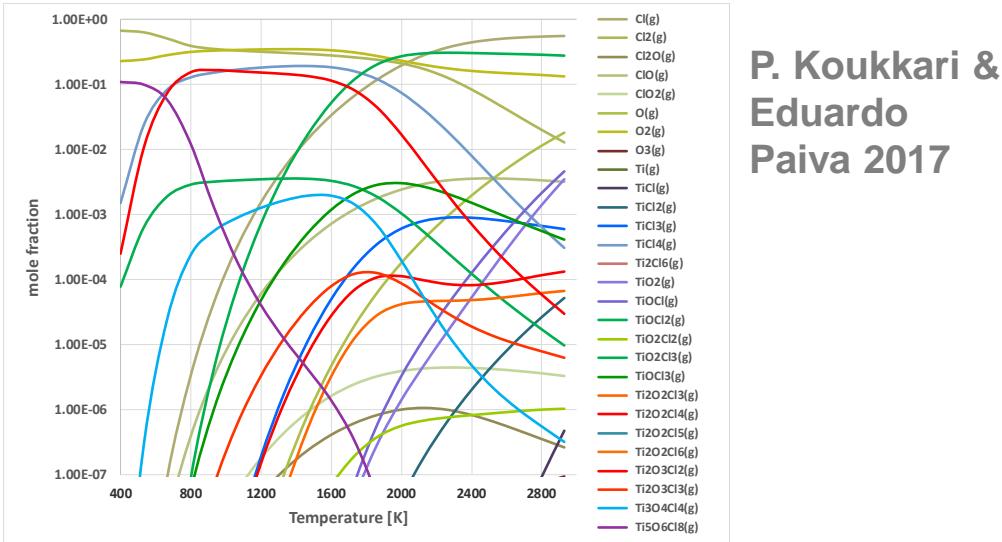
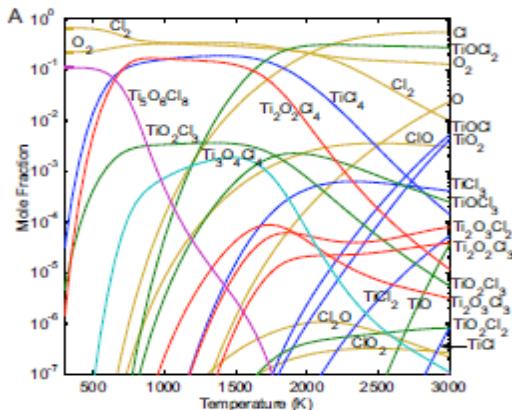
GAS PHASE, P = 3 BAR; T = 1500 K;  $TiCl_4: O_2 \sim 1:1$

ALL SPECIES



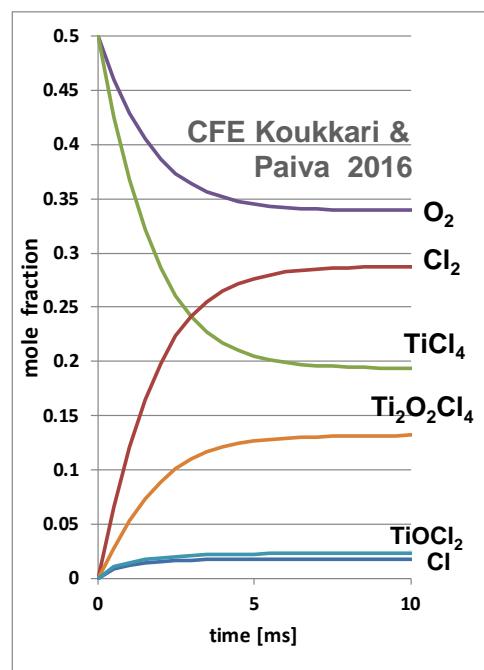
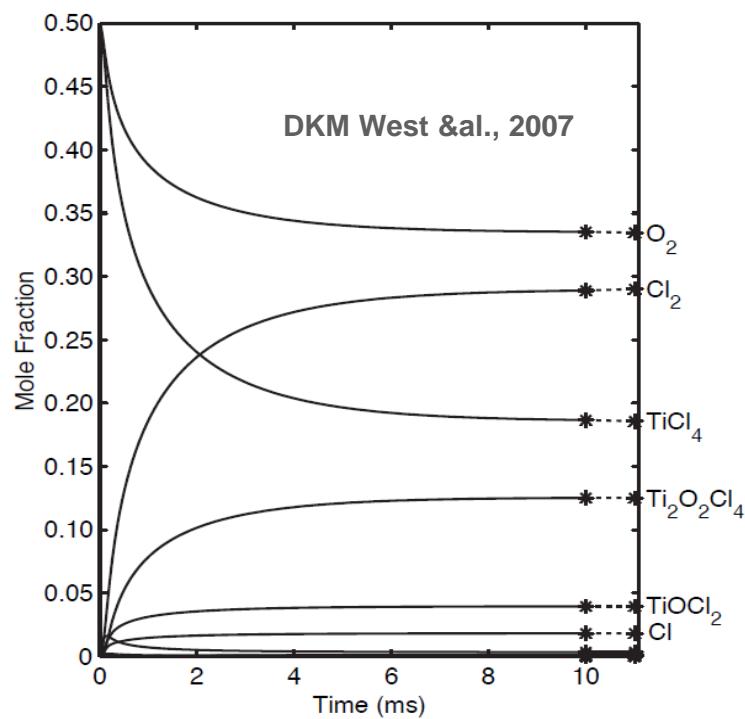
West & al.  
2007

*J. Phys. Chem. A* 2007, 111, 3560–3565



P. Koukkari &  
Eduardo  
Paiva 2017

# COMPARISON OF DKM AND CFE KINETIC CALCULATION MAJOR SPECIES



**TiCl<sub>4</sub> conversion constraint:**

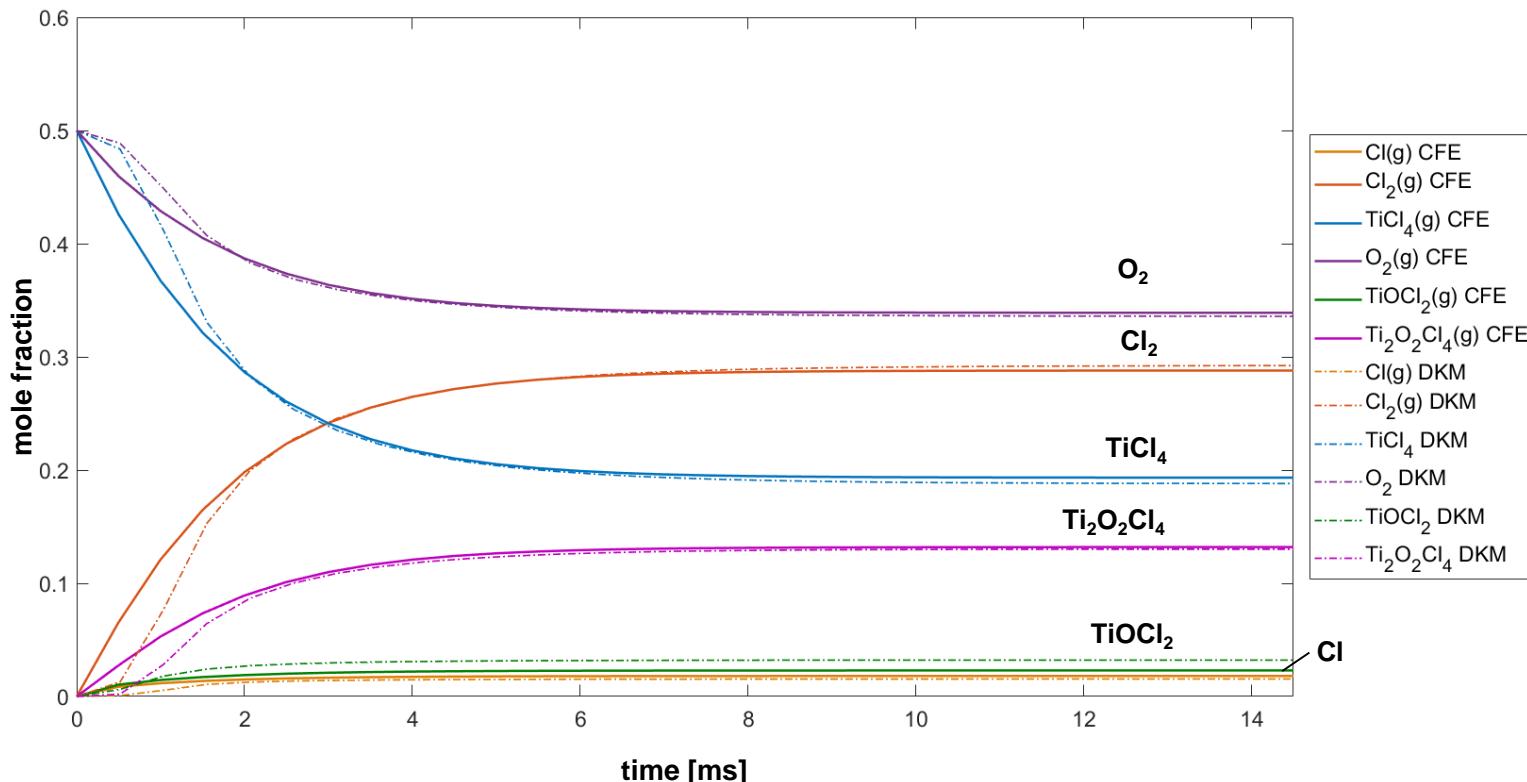
$$\frac{d [TiCl_4]}{dt} = -k [TiCl_4] ;$$

$$k = A \exp\left[\frac{-71.0 \text{ kJ/mol}}{RT}\right]$$

$$A = 8.26 \cdot 10^4 \text{ s}^{-1}$$

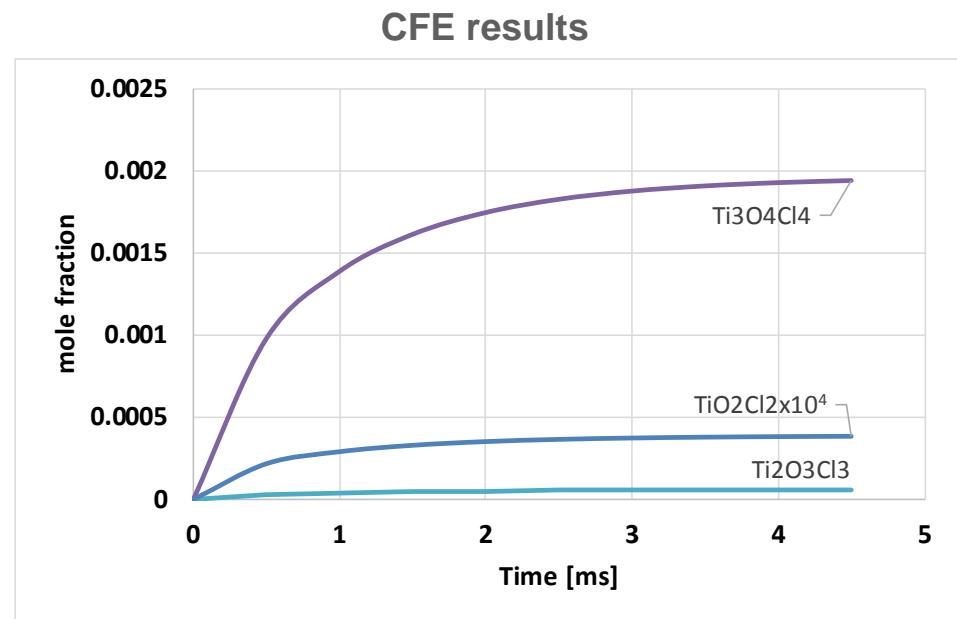
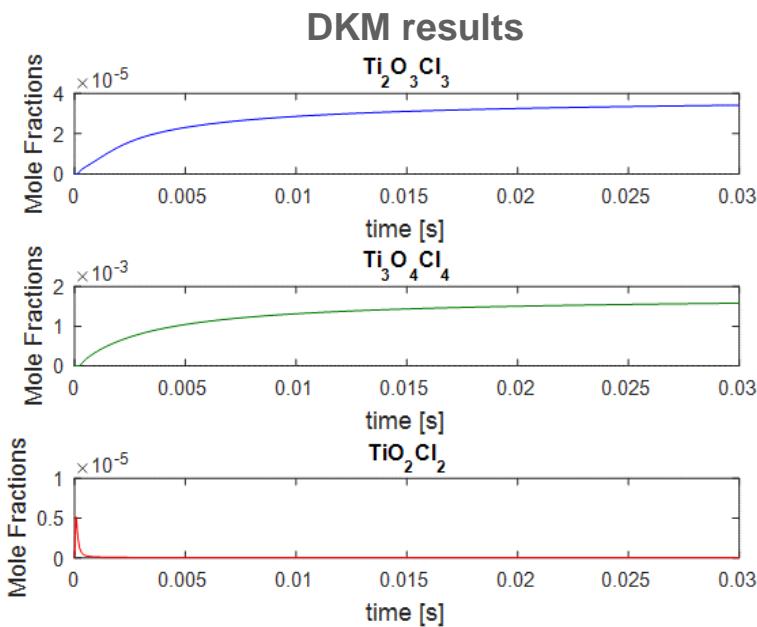
Data from  
Koukkari & Liukkonen  
Ind. Eng. Chem. Res.,  
41 (2002) 2931.

# COMPARISON OF DKM AND CFE KINETIC CALCULATION MAJOR SPECIES



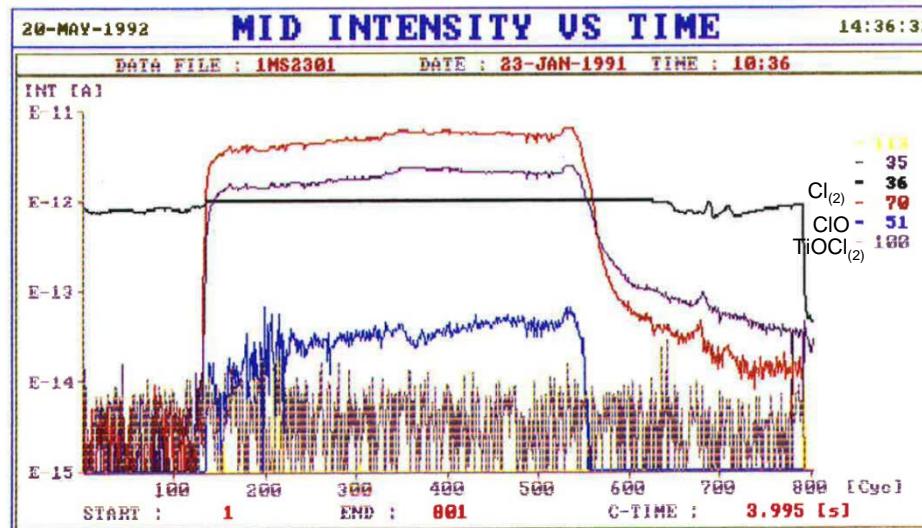
- With only gas phase included, the two models appear in close agreement
- Kinetics of major gaseous species generally used for aerosol nanoparticle modelling (studies on nucleation and population balance)

# COMPARISON OF DKM AND CFE KINETIC CALCULATION MINOR SPECIES (SELECTION)



- minor species monotonically ascending in CFE (unless additional constraints are applied)
- (no experimental data for detailed kinetics exist)

- DKM and CFE give congruent results for the (gas phase) kinetics
- How about model vs. experiments ?



Karlemo & al., Plasma Chem .& Plasma Proc. 16, (1996) 59.

# EXPERIMENTAL ARRHENIUS PLOT FOR $\text{TiCl}_4$ CONSUMPTION

□ Plug flow reactor measurements of  $\text{TiCl}_4$  consumption with various residence times (700-900 C)

□  $\Rightarrow$  effective rate constant  $k_{eff} = A \cdot \exp(-E_a/RT)$   $E_a \sim 101 \text{ kJ} \cdot \text{mol}^{-1}$ ;  $A = 1.59 \cdot 10^5 \text{ s}^{-1}$ ; ( $\text{TiCl}_4 : \text{O}_2 \sim 1 : 5$ )

$[\text{TiCl}_4]$  data as  $c_o$ ;  $c_i = c_i(t)$

$$-\left( \ln\left(\frac{c_o}{c_i}\right) / t \right) = k_{eff}$$

$$k_{eff} = f(T);$$

independent of residence time

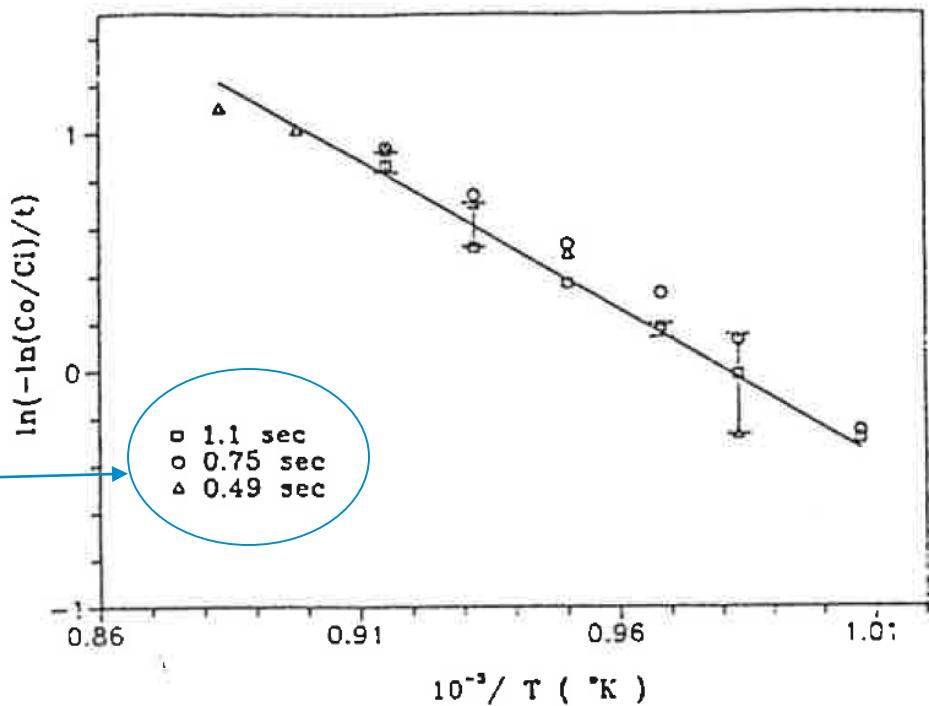


Fig. 4. Arrhenius plot of the oxidation rate of  $\text{TiCl}_4$ .

# GAS PHASE MODELS CHECKED WITH EXPERIMENT

## ARRHENIUS PLOT\*

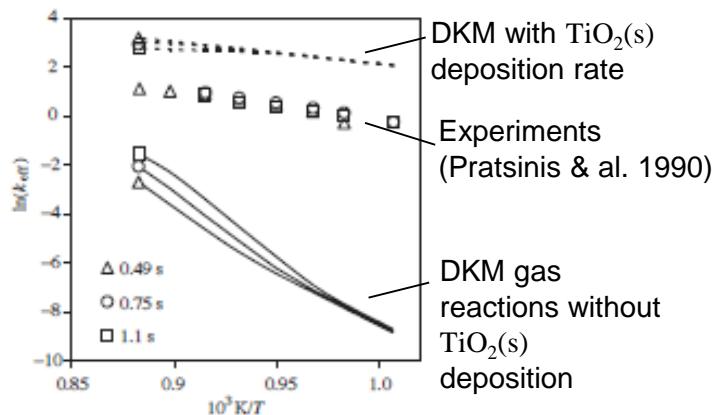
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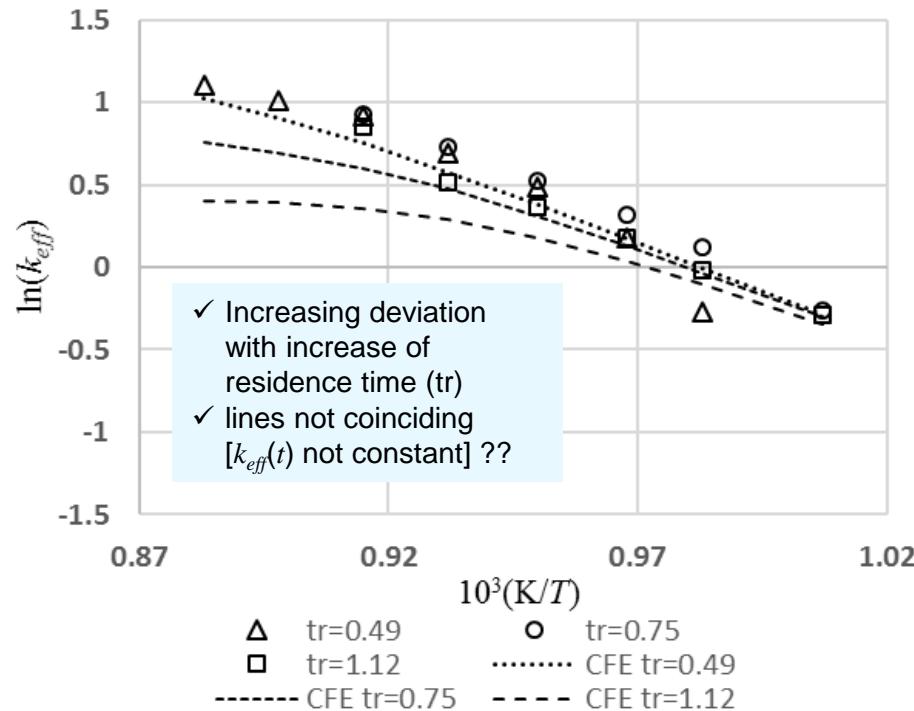
$[\text{TiCl}_4]$  data as  $c_o$ ;  $c_i = c_i(t)$

$$-\left( \ln\left(\frac{c_o}{c_i}\right) / t \right) = k_{eff}$$

DKM West & al., 2008



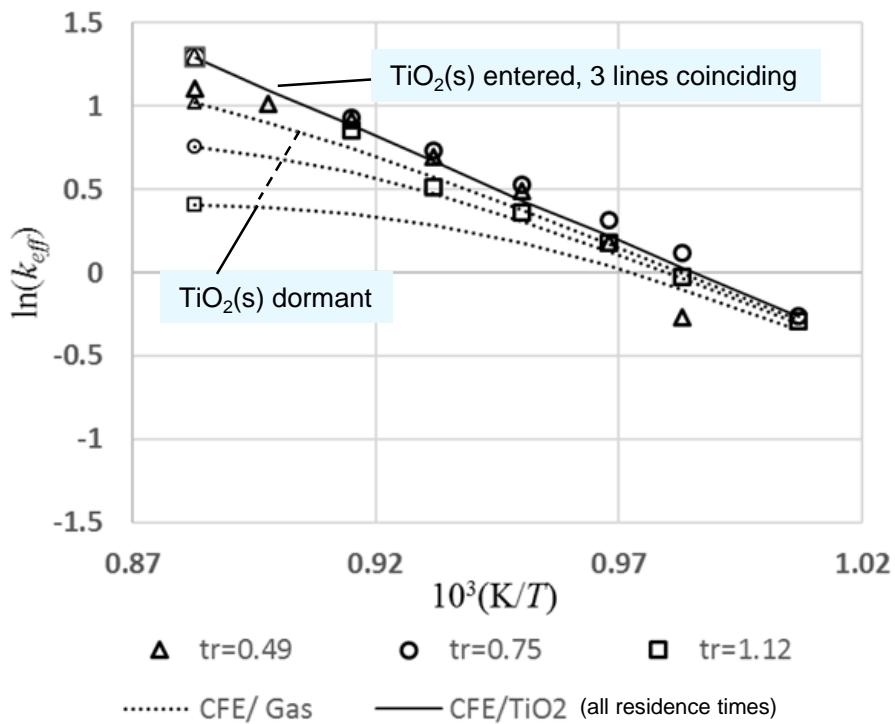
Gas phase CFE calculations cross-checked with experiment



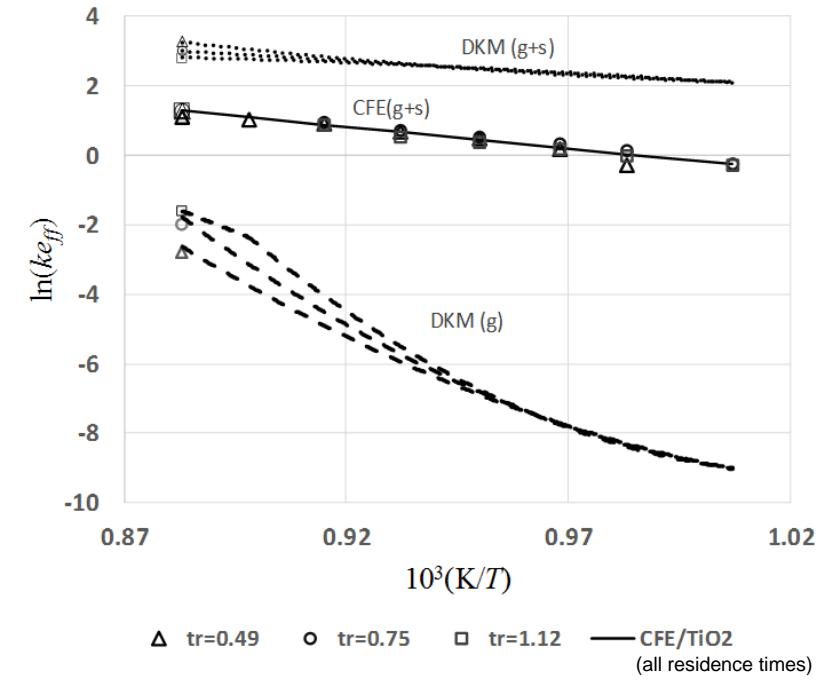
\*Pratsinis, J.Am.Ceram.Soc. 1990, 73, 7, 2158-62

# CFE RESULTS WITH $\text{TiO}_2(\text{s})$ FORMATION

CFE Koukkari & Paiva 2017

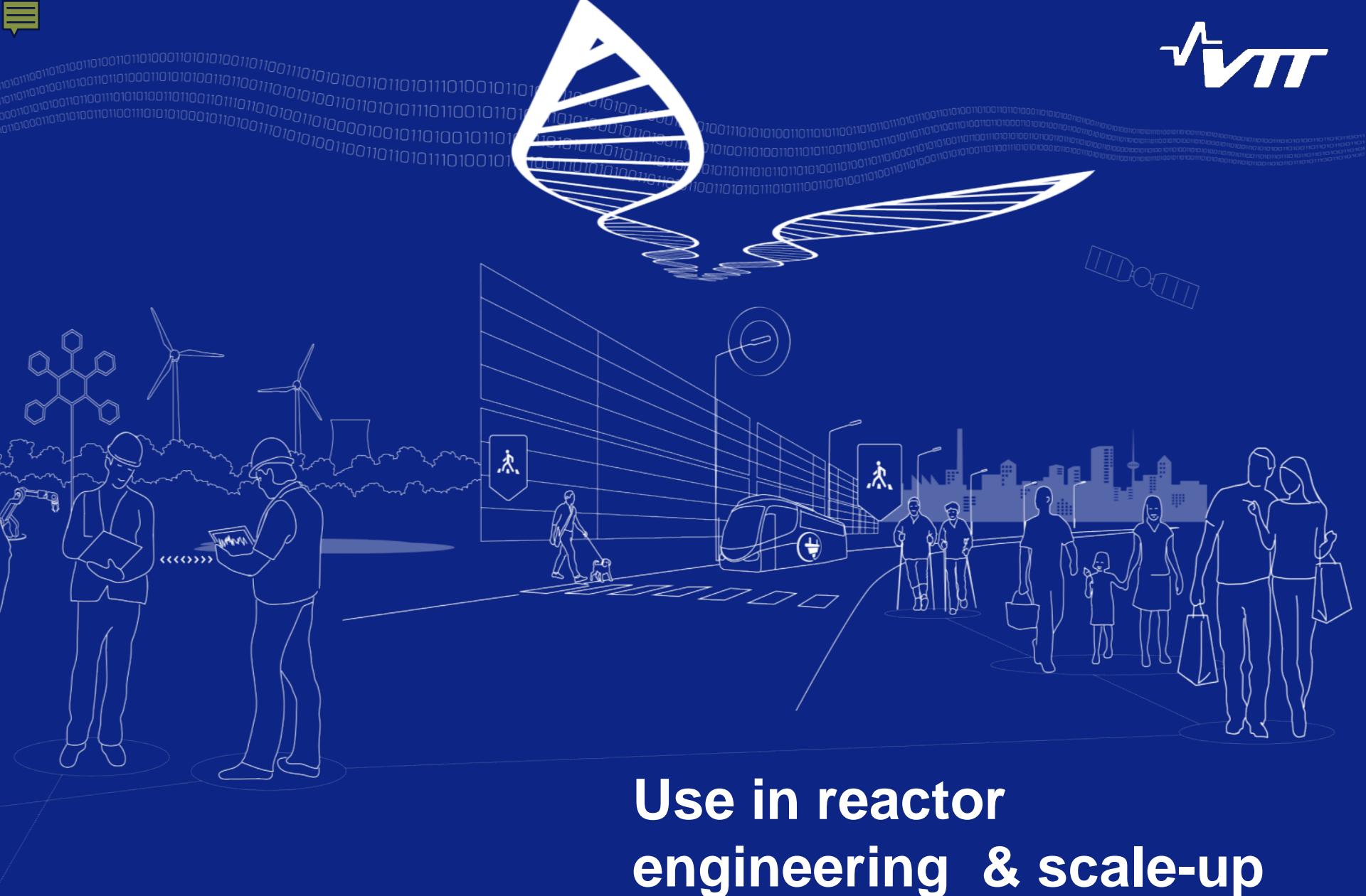


CFE \_ DKM comparison



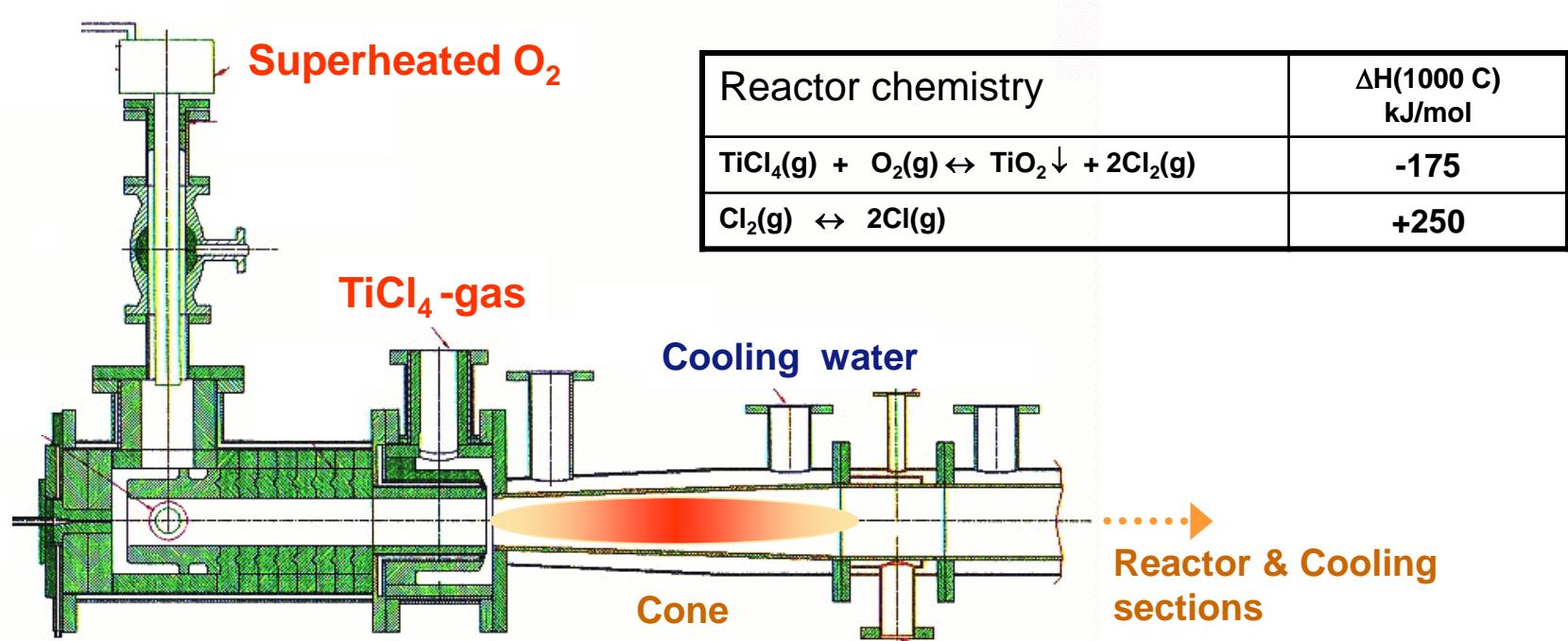
☐ Experiments only followed  $\text{TiCl}_4$  concentrations in gas phase

⇒  $\text{TiO}_2(\text{s})$  '**entered**' seems to be the necessary & sufficient condition for agreement with observation



# Use in reactor engineering & scale-up

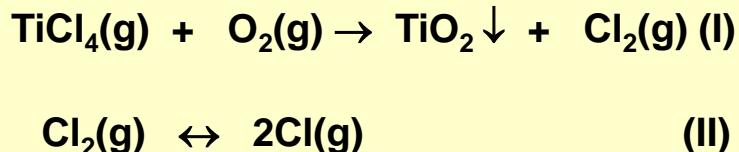
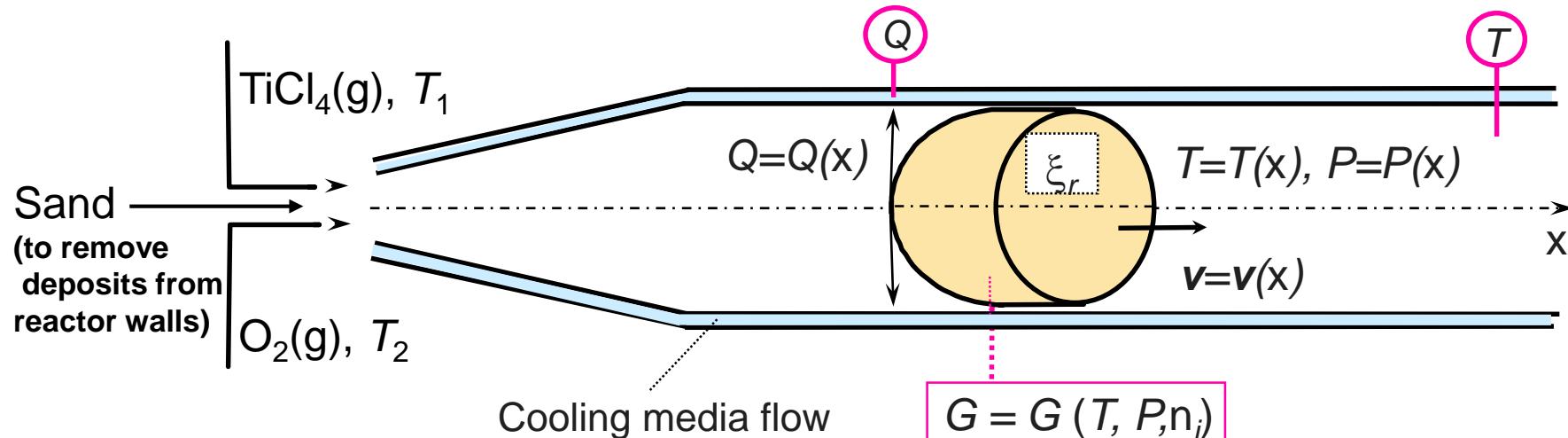
# Flame reactor scale-up with the rate-constrained model



- TiO<sub>2</sub> is formed as a nanoparticle suspension – used as the white pigment (> 3 Mt/yr)
- exothermic main reaction compensated by endothermic side reactions (chlorine dissociation, Ti<sub>x</sub>O<sub>y</sub>Cl<sub>z</sub> formation) and efficient reactor cooling

Objective: Perform reactor scale-up with good coupling of thermochemistry and reaction kinetics and validate the model

# Build-up of the industrial $\text{TiCl}_4$ -oxidiser model



Gibbs energy ('HSC') data available for all species

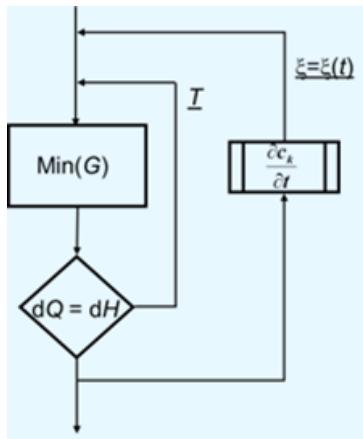
$$Q = \frac{\pi \cdot d_o \cdot h \cdot (T_a - T_g)}{\frac{d_o}{h_i \cdot d_i} + \frac{d_o}{2 \cdot \lambda_w} \ln \frac{d_o}{d_i} + \frac{1}{h_o}}$$

Reaction	$\Delta H$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta G$ $\text{kJ}\cdot\text{mol}^{-1}$	Reaction rate equation *	$E_a$ $\text{kJ}\cdot\text{mol}^{-1}$	$A$ $\text{s}^{-1}$	$A'$ $(\text{dm}^3\cdot\text{mol}^{-1})^{1/2}\cdot\text{s}^{-1}$
(I)	-175.4	-104.1	$\frac{d[\text{TiCl}_4]}{dt} = - (k + k' \sqrt{[\text{O}_2]}) [\text{TiCl}_4]$	~ 71	$8.26 \cdot 10^4$	$1.4 \cdot 10^5$
(II)	250.3	98.2	assumed equilibrium	-	-	-

\*  $\text{TiCl}_4$  consumption rate measured by Pratsinis & al., 1990

# VALIDATION OF NON-ISOTHERMAL SCALE-UP CALCULATIONS

Choice of independent measurables for model validation:

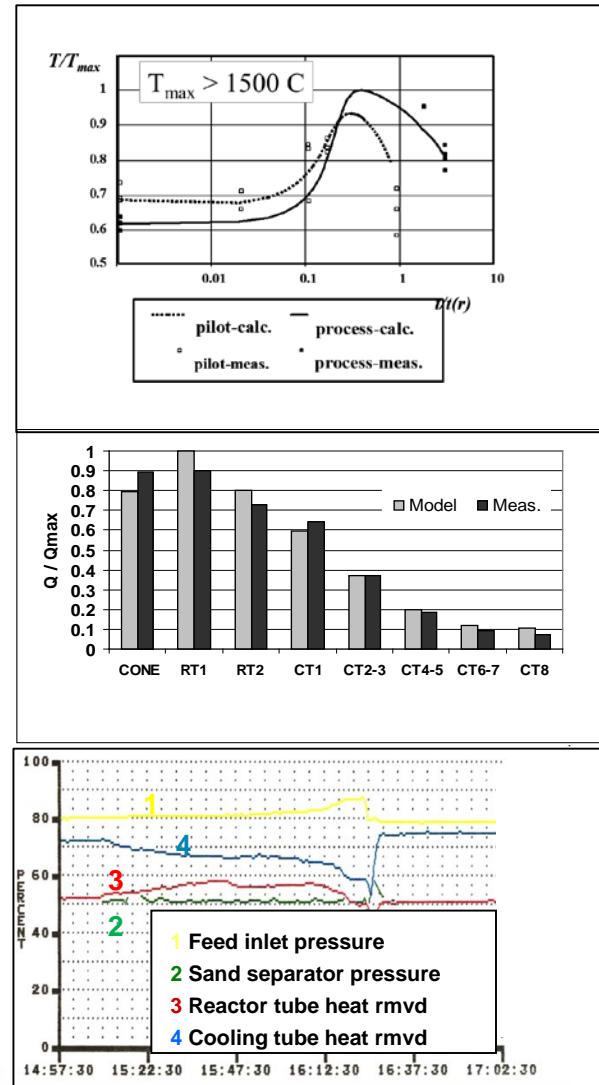


- direct temperature measurement  
(2 plug flow reactors)

- heat transfer measurement from  
the tubular reactor

- plant historical trends for  
direct & indirect checks

CFE scale-up performed for 2 industrial pigment producers  
(US & NL)



# CONCLUSIONS

- ❑ Immaterial constraints can be introduced to Gibbs energy minimization to allow the calculation of kinetically controlled systems
- ❑ reaction matrix serves as basis for new constraints for reaction extents
- ❑ stoichiometric matrix includes all reactions
- ❑ ⇒ CFE provides a viable and robust alternative for mechanistic kinetic studies in complex multi-component – multi-phase systems; has also small number of kinetic parameters
- ❑ Assuming local chemical equilibrium (LCE) with  $\text{TiO}_2(\text{s})$  formation agrees with plug flow experiments – encourages more research on CFE/LCE method of multiphase systems

# Published applications of the G( $\xi$ ) [Ratemix\*] method

Methanation  
 $TiO_2$  production  
Combustion  
In-line PCC production  
Clinker formation in cement kilns  
Phase equilibria during steel solidification

Extent of methanation reactions  
Oxidation of  $TiCl_4$  in furnace  
Post-flame NO<sub>x</sub> generation  
Precipitation of  $CaCO_3$   
Formation of C<sub>2,3</sub>S-phases & free lime (cement making)  
Paraequilibrium phase diagrams

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**Computation of steady state thermochemistry in rotary kilns: Application to the cement clinker manufacturing process**

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Para-equilibrium phase diagrams

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\*Ratemix is a trademark of VTT





**Thank you for  
your attention !**