

# Applying the driving force and extent of reaction as phase diagram axis

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- Overview of the Constrained Free Energy minimisation method (CFE)
- Phase diagrams for constrained systems
  - Surface phases and paraequilibria
  - Driving force and reaction advancement as variables
  - Examples of diagrams with new axis

# Overview of the CFE method

- Gibbs'ian methods well established for complex global equilibria and equilibrium phase diagrams. Necessary constraints for conventional  $\min(G)$  are set for T, P and amounts of components (molecular mass balance)
- $\min(G)$  methods generally do not include thermodynamic work or time-dependency
- Constrained Gibbs free energy (CFE) minimisation deals with complex systems affected either by generalised work terms or reaction kinetics
- CFE is applied by using massless conditions as the necessary conservation constraints for various work terms and/or extent of chemical reaction ( $\xi$ ). The massless conditions appear in the input matrix generally as virtual components and virtual phases (with zero mass).

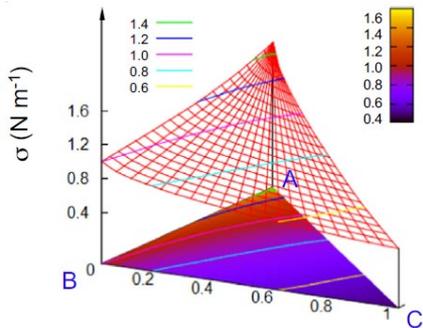
$$dG = -SdT + VdP - \sum_j^{\text{other work terms}} l_j dL_j + \sum_{k=1}^N \mu_k dn_k - Dd\xi$$

⇒ CFE also allows for construction of non-conventional phase diagrams



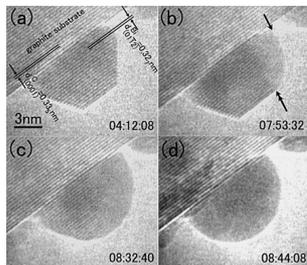
# Published phase diagrams using constrained min(G)

## Surface energy



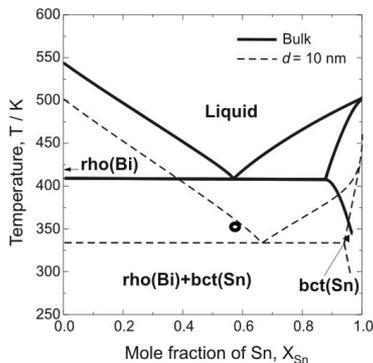
Kang Y-B. 2015. Calphad 50, 23-31

## Alloy nano-particles

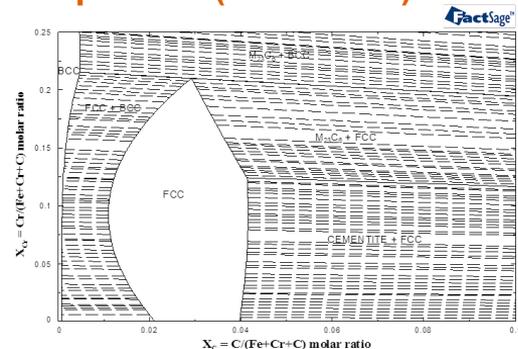


Lee J, Lee J-H, Tanaka T, Mori H, Penttilä K. 2005. JOM-J Min. Met. Mat. S. 57, 56-59.

Pajarre R, Koukkari P, Kangas P. 2016. CES\_146, 244-258.



## Diffusionless para-equilibria (steels etc.)

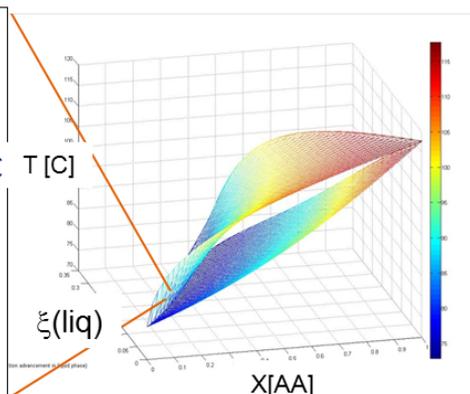
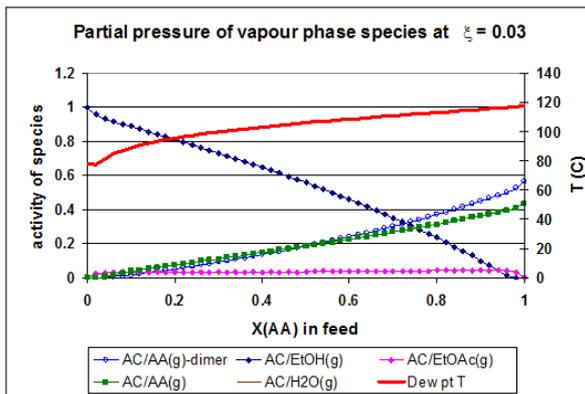


Pelton A, Koukkari P, Pajarre R, Eriksson G. 2014. J. Chem. Thermodynamics 72 16–22.

## The reactive ethanol-acetic acid system:



Koukkari P, Pajarre R, Blomberg P. 2011. Pure Appl.Chem. 83(5), 1063-1074



'Early bird' version using ChemSheet and MatLab software where  $\xi$  is the EOR of esterification reaction in the acetic acid-ethanol system



# Conditions and variables for phase diagrams

Gibbs Free Energy:

$$dG = -SdT + VdP + \sum_{j=1}^{NC} \mu_j dN_j - Dd\xi$$

$D = 0$  at equilibrium

System of NC components:

- choose n potentials for the diagrams ( $n < NC+1$ ), including  $T, P, \mu_j$
- form  $NC+1-n$  independent ratios of the non-corresponding extensive variables (e.g. amounts of components)
- out of these  $NC+1$  variables may be used, two chosen as independent variables for XY-axis and the remainder must be held constant
  - ⇒ Non-equilibrium affinity ( $D_r = A_r$ ) may appear as potential,  $\xi_r = \text{EOR}^*$  as extensive variable (must be related to some other quantity)
  - ⇒ EOR is a given (input) amount of the virtual phase, affinity is received from the activity of the virtual component

\* *Extent of a chemical reaction*



# Inclusion studies for continuous casting of steels

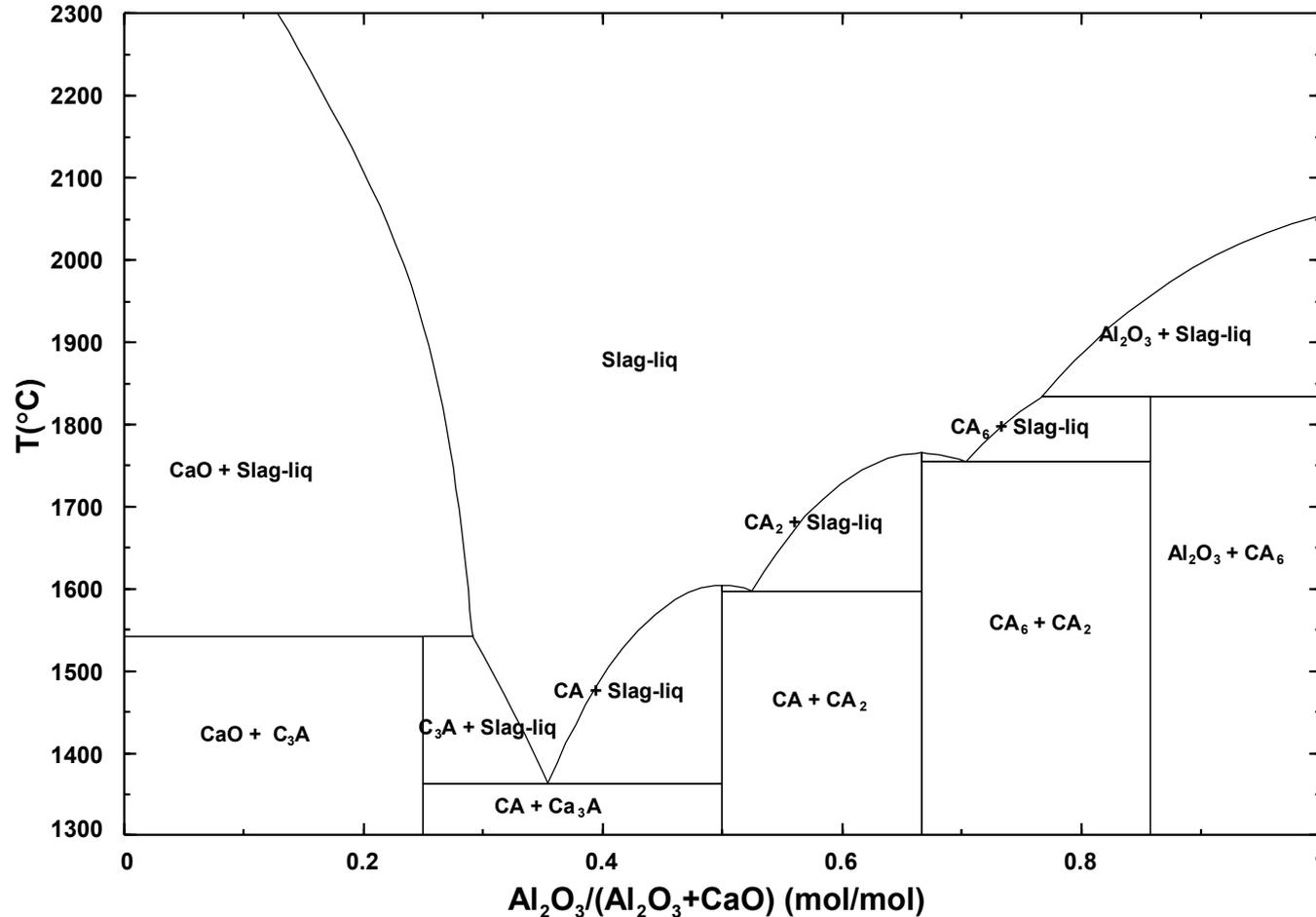


- raw steel is 'doped' with e.g. Calcium and Aluminium to improve machinability and grain refining in the product, Sulphur for e.g. increased strength
- non-metallic impurities from Ca, Al, S may react to form (often) undesired solid phases during solidification
- these solid phases may cause nozzle clogging in continuous casting
- the solid inclusions often analysed with diffusion models such as IDS\*

\*Interdendritic solidification model,  
Holappa, L. & al 6th Int.Conf.on Clean Steel, Balatonfured, Hungary, 10-12 June 2002



# Equilibrium phase diagram for the CaO-Al<sub>2</sub>O<sub>3</sub> system



- Calcium-Aluminium compounds at equilibrium
- Liquidus depends of Al\_Ca-ratio
- Respective phases should be analysed during the course of steel solidification
- For this purpose a CFE steel solidification procedure was applied



# Constraint set for solid Fe-phase formation

Thermodynamic System

System properties:

- System
  - Components
    - Fe
    - Mn
    - Cr
    - Ti
    - Ca
    - S
    - Si
    - Al
    - Mg
    - O
    - C
    - v1**
  - Constraints
    - Mixture phases
    - Pure phases

Selection properties:

Name	Value
Name	v1
Molar weight/g/mol	0.00001

Mn21104(S2)  
Fe\_bcc  
1.00000 moles of Fe  
1.00000 moles of v1  
Fe\_fcc  
Fe203\_hematite(S1)  
Fe203\_hematite(S2)  
Fe304\_magnetite(S1)  
Fe304\_magnetite(S2)  
(MgO)(Fe203)

ENTERED  
ENTERED

- (FeO)2(TiO2)\_ulvospinel
- Fe205Ti\_ferric-pseud
- (MnO)(Fe203)
- r1

ENTE  
ENTE Selection properties:

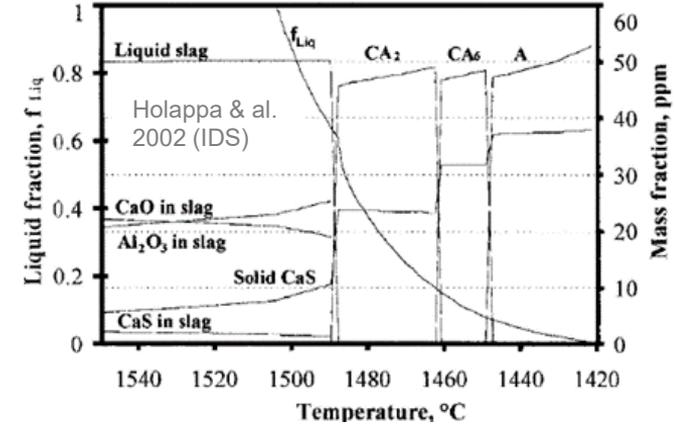
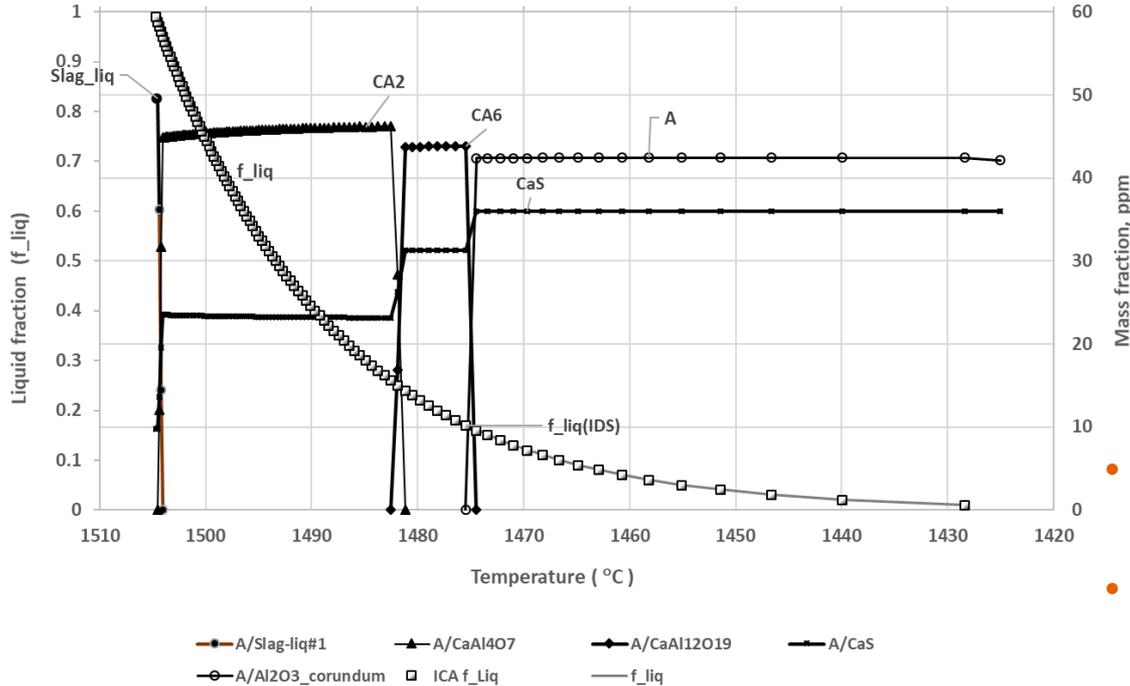
Name	V...
Number of phases	145
Number of constituents	145

- Massless virtual component (v1) applied as virtual constraint for BCC and FCC solid iron – respective virtual phase denoted as  $r_1$
- Controlling input of this virtual component the extent of Fe-solidification ( $\xi$ ) can be followed
- $\xi$  can be a function of time and/or temperature

Virtual component (v1) has negligible (zero) mass



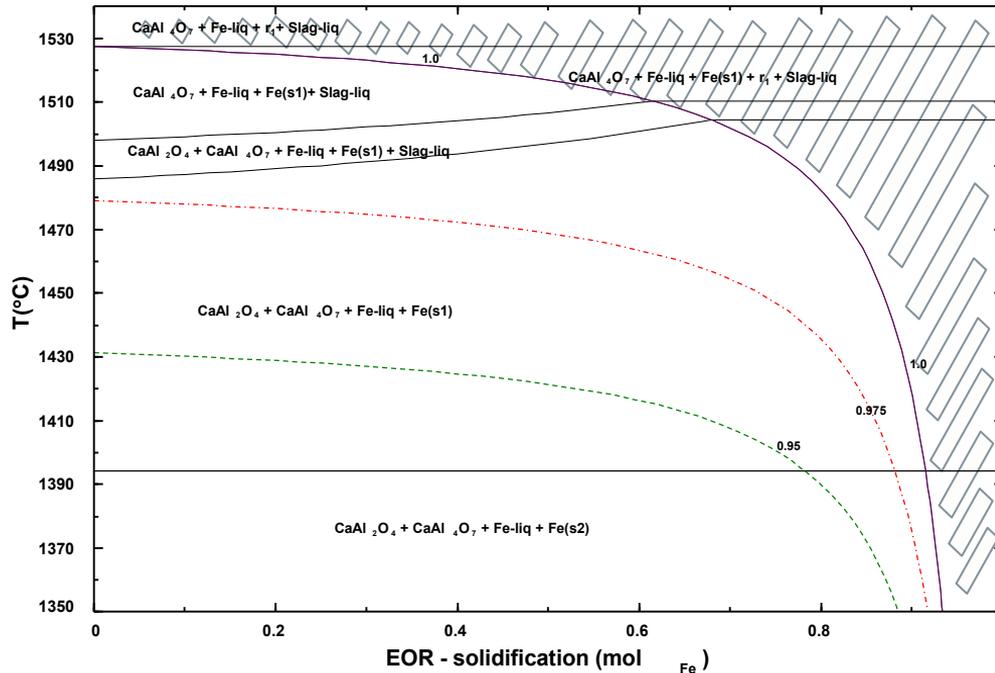
# CFE Chemsheet inclusion model compared with IDS



- Solidification rate adapted to ChemSheet-CFE from the IDS-model
- Partial equilibria assumed for inclusion phases (CA<sub>2</sub>, CA<sub>6</sub>, A as well as CaS) in fair agreement with IDS results
- No kinetics assumed for the inclusion phases in CFE (IDS has kinetics, not published)

Partial equilibria of oxide and sulphide inclusions in steel solidification with composition C 0.35 %, Si 0.25 %, S 0.25 %, O 20 ppm, Ca 20 and Al 200 ppm.

# FactSage T, $\xi$ -diagram for CA-inclusion phases

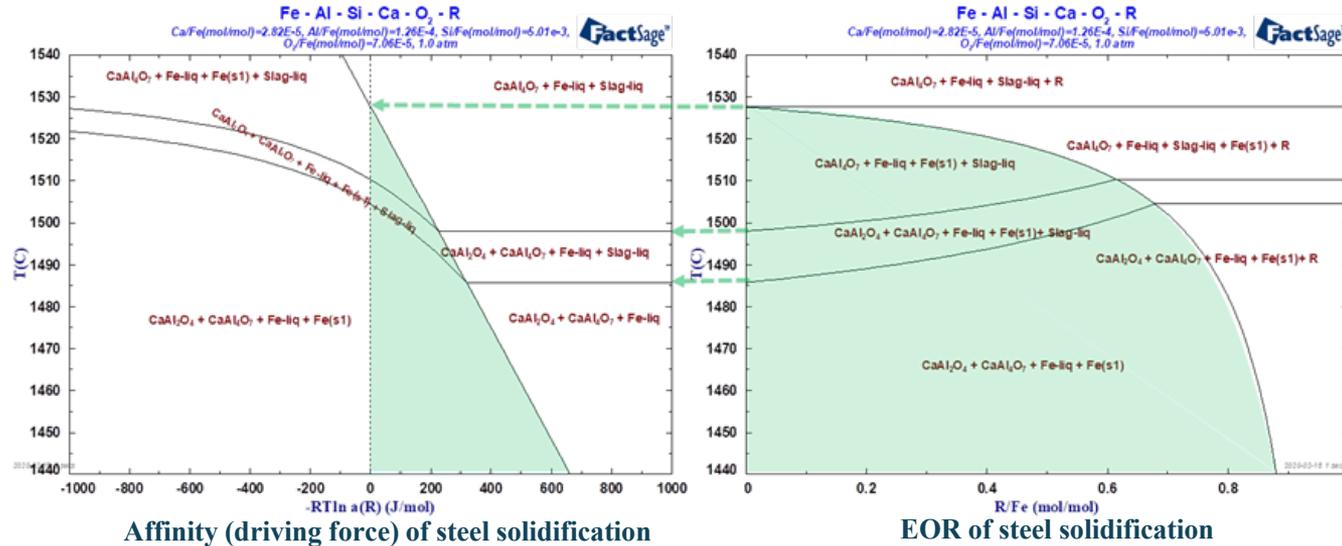


Molar ratios  $O_2/Fe=7.06E-5$ ,  $Al/Fe=1.26E-4$ ,  $Si/Fe=5.01e-3$ ,  $Ca/Fe=2.82E-5$ .

- Extent of solidification ( $\xi$ , related to total Fe) used as axis for a non-equilibrium phase diagram
- Solid lines indicate the (partial) equilibrium phase boundaries
- The dotted and dash-dotted lines represent iso-activities of the virtual phase  $r_1$
- The striped area with stable  $r_1$ -phase exceeds the equilibrium limit of solid and liquid iron - corresponds to the superheated solid in a reverse (melting) process
- Diagram is an easy-to-use tool for studying inclusion formation as partial equilibrium phases
- No kinetic assumptions or parameters



# T,ξ-diagram and T,D-diagram compared

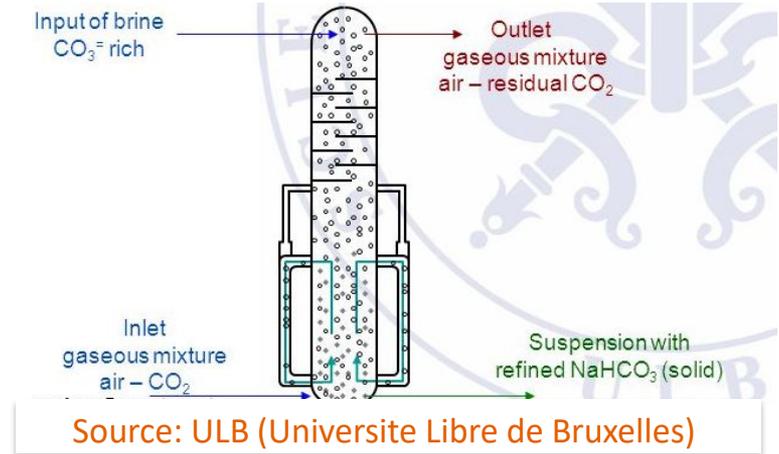


- in the T,D-potential diagram (left) the solid lines indicate co-existence of phases at equilibrium
- Fe(s)-Fe(liq) -equilibrium in the potential diagram is at the zero affinity vertical line in the middle
- The shaded areas represent the undercooling sections of the solidification process.
- The inclusion (Ca-aluminate) phases are shown in both diagrams according to their partial equilibrium stability.



# Example of an aqueous system

- In the Solvay BIR process  $\text{CO}_2$  is absorbed to a sodium carbonate solution
- Sodium bicarbonate ( $\text{NaHCO}_3$ ) is formed in the overall reaction:
- $\text{Na}_2\text{CO}_3(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O} \Leftrightarrow \text{NaHCO}_3\downarrow$
- absorption rate of  $\text{CO}_2(\text{g}) \Rightarrow \text{CO}_2(\text{aq})$  is deemed critical
- Use a phase diagram studies
  - aqueous phase equilibrium
  - state of the solution and phase formation as function of the extent of the  $\text{CO}_2$  absorption

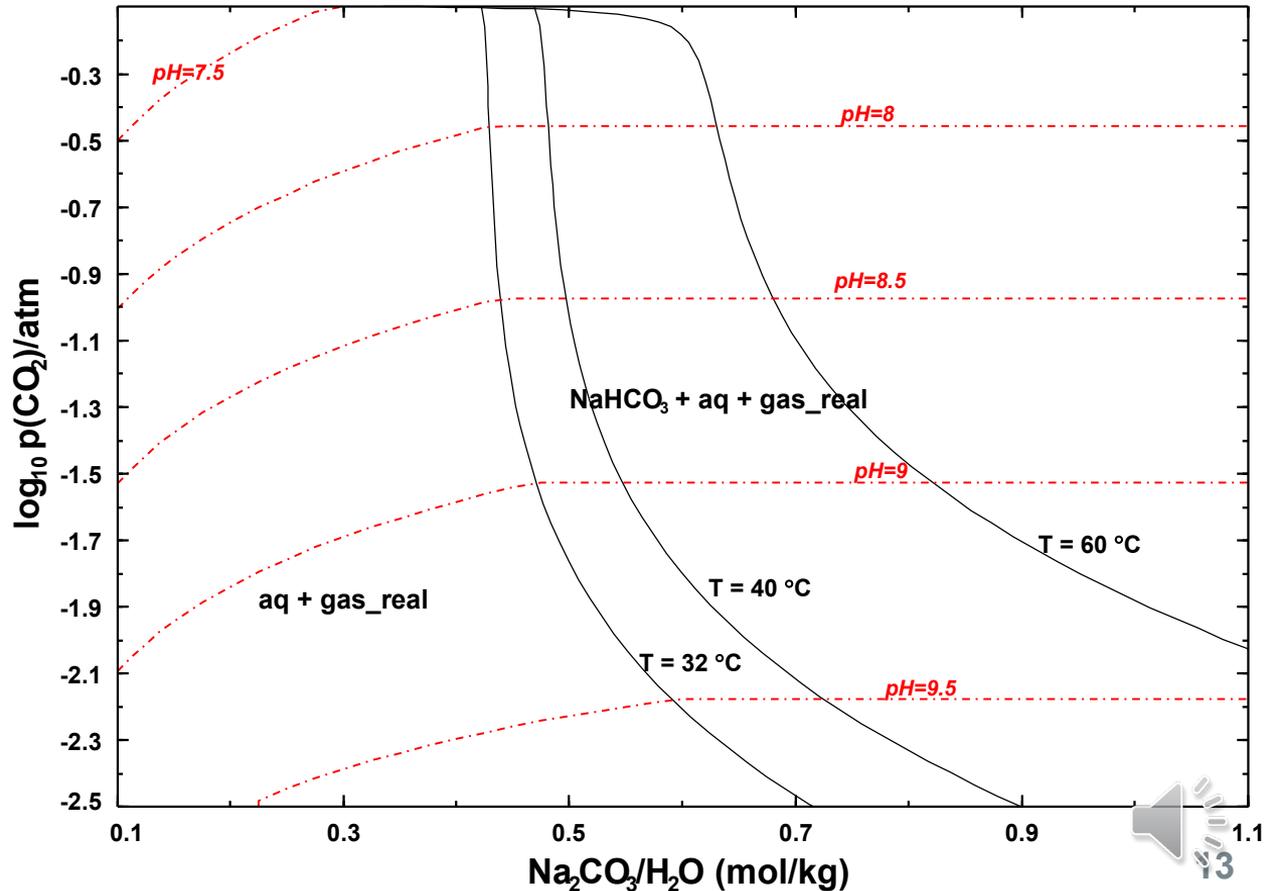


# Equilibrium phase diagram for the CO<sub>2</sub>-H<sub>2</sub>O-Na<sub>2</sub>CO<sub>3</sub> system

## System:

	N	O	C	H	Na	EA
N <sub>2</sub> (g)	2	0	0	0	0	0
O <sub>2</sub> (g)	0	2	0	0	0	0
CO <sub>2</sub> (g)	0	2	1	0	0	0
H <sub>2</sub> O(g)	0	1	0	2	0	0
H <sub>2</sub> O	0	1	0	2	0	0
H <sup>+</sup>	0	0	0	1	0	-1
OH <sup>-</sup>	0	1	0	1	0	1
CO <sub>2</sub> (aq)	0	2	1	0	0	0
HCO <sub>3</sub> <sup>-</sup>	0	3	1	1	0	1
CO <sub>3</sub> <sup>2-</sup>	0	3	1	0	0	2
Na <sup>+</sup>	0	0	0	0	1	-1
Na <sub>2</sub> CO <sub>3</sub>	0	3	1	0	2	0
NaOH	0	1	0	1	1	0
NaHCO <sub>3</sub>	0	3	1	1	1	0

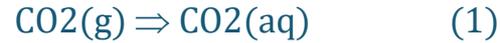
- NaHCO<sub>3</sub> solubility increases with increasing temperature
- Increasing P(CO<sub>2</sub>):
  - leads to NaHCO<sub>3</sub> formation
  - decreases pH



# EOR -constraints for CO<sub>2</sub> absorption and NaHCO<sub>3</sub> formation

	N	O	C	H	Na	EA	$v_1$	$v_2$
N <sub>2</sub> (g)	2	0	0	0	0	0	0	0
O <sub>2</sub> (g)	0	2	0	0	0	0	0	0
CO <sub>2</sub> (g)	0	2	1	0	0	0	1	0
H <sub>2</sub> O(g)	0	1	0	2	0	0	0	0
H <sub>2</sub> O	0	1	0	2	0	0	0	0
H <sup>+</sup>	0	0	0	1	0	-1	0	0
OH <sup>-</sup>	0	1	0	1	0	1	0	0
CO <sub>2</sub> (aq)	0	2	1	0	0	0	0	0
HCO <sub>3</sub> <sup>-</sup>	0	3	1	1	0	1	0	0
CO <sub>3</sub> <sup>2-</sup>	0	3	1	0	0	2	0	0
Na <sup>+</sup>	0	0	0	0	1	-1	0	0
Na <sub>2</sub> CO <sub>3</sub>	0	3	1	0	2	0	0	0
NaOH	0	1	0	1	1	0	0	0
NaHCO <sub>3</sub>	0	3	1	1	1	0	0	1
$r_1^+$	0	0	0	0	0	0	1	0
$r_1^-$	0	0	0	0	0	0	-1	0
$r_2^+$	0	0	0	0	0	0	0	1
$r_2^-$	0	0	0	0	0	0	0	-1

Constrained reactions with virtual components  $v_1$  and  $v_2$ :



Constraints affect either products or reactants:

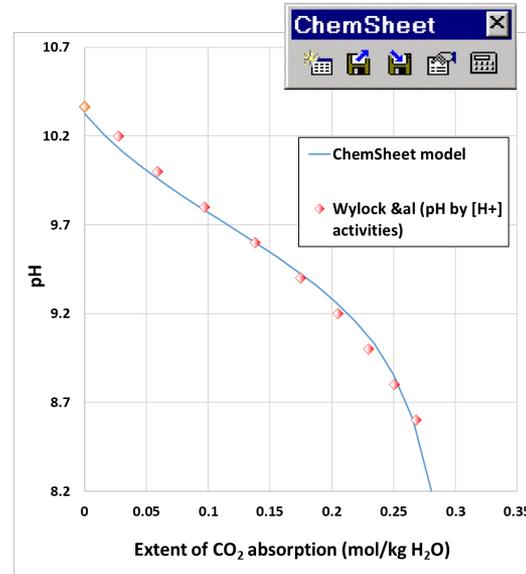
respectively, forward or reverse reactions can be constrained

Note: if only positive elements can be used for the applied software, only products of each reaction can then be affected

# EOR -constraints for CO<sub>2</sub> absorption and NaHCO<sub>3</sub> formation

	N	O	C	H	Na	EA	$v_1$	
N <sub>2</sub> (g)	2	0	0	0	0	0	0	0
O <sub>2</sub> (g)	0	2	0	0	0	0	0	0
CO <sub>2</sub> (g)	0	2	1	0	0	0	1	0
H <sub>2</sub> O(g)	0	1	0	2	0	0	0	0
H <sub>2</sub> O	0	1	0	2	0	0	0	0
H <sup>+</sup>	0	0	0	1	0	-1	0	0
OH <sup>-</sup>	0	1	0	1	0	1	0	0
CO <sub>2</sub> (aq)	0	2	1	0	0	0	0	0
HCO <sub>3</sub> <sup>-</sup>	0	3	1	1	0	1	0	0
CO <sub>3</sub> <sup>2-</sup>	0	3	1	0	0	2	0	0
Na <sup>+</sup>	0	0	0	0	1	-1	0	0
Na <sub>2</sub> CO <sub>3</sub>	0	3	1	0	2	0	0	0
NaOH	0	1	0	1	1	0	0	0
NaHCO <sub>3</sub>	0	3	1	1	1	0	0	1
$r_1^+$	0	0	0	0	0	0	1	0
$r_1^-$	0	0	0	0	0	0	-1	0
$r_2^+$	0	0	0	0	0	0	0	1
$r_2^-$	0	0	0	0	0	0	0	-1

Constrained reactions with virtual components  $v_1$  and  $v_2$ :

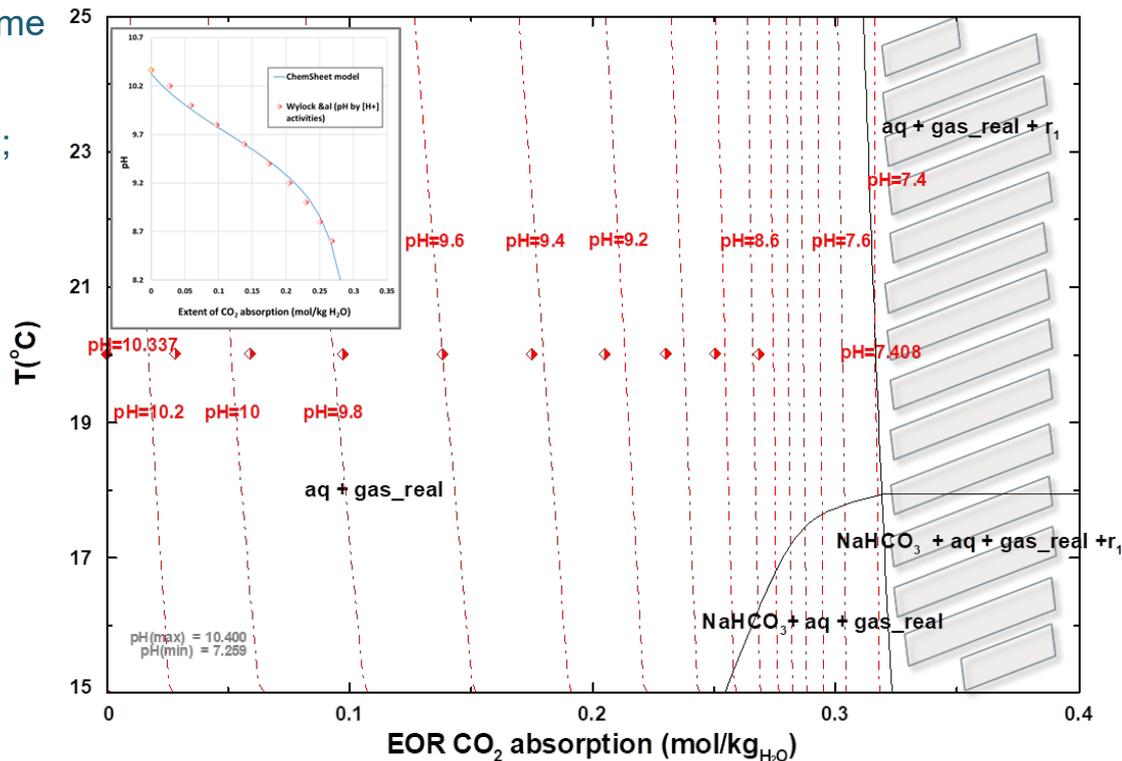


Partial equilibrium CFE model:

- Constraint only for reaction (1), no time-dependent kinetics
- 0.283 m Na<sub>2</sub>CO<sub>3</sub> and 0.226 m NaHCO<sub>3</sub> in the solution
- T = 20 C, P(CO<sub>2</sub>) = 1 atm
- pH vs EOR of CO<sub>2</sub> absorption compared with measured results (Wylock & al, 2008 converted to [H<sup>+</sup>] activity scale)

# T, $\xi$ - phase diagram for the CO<sub>2</sub>-H<sub>2</sub>O-Na<sub>2</sub>CO<sub>3</sub> absorption system

- Reaction (1) constrained (CO<sub>2</sub>-absorption, same input conditions as in the ChemSheet model)
- Affinity of reaction (2) set to zero (equilibrium); solubility limit of NaHCO<sub>3</sub> is seen by the phase boundaries (solid lines)
- Intermediate iso-pH lines are calculated assuming no other kinetic restriction than extent of reaction (EOR) of CO<sub>2</sub>-absorption
- Under this assumption the iso-pH lines may be used to indicate advancement of the CO<sub>2</sub> absorption
- The striped area to the right exceeding the equilibrium limit of CO<sub>2</sub>-absorption shows the 'virtual phase r<sub>1</sub> appearing as stable\*.



\*This non-physical condition could be avoided by setting the virtual phase r<sub>1</sub> dormant and the result would then show the supersaturated solution condition

virtual component (v1) related to amount of water

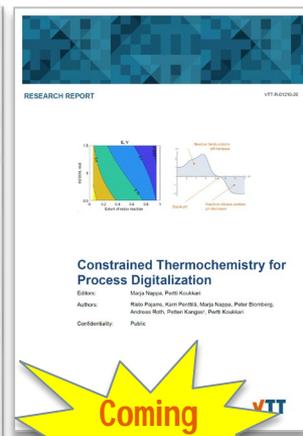
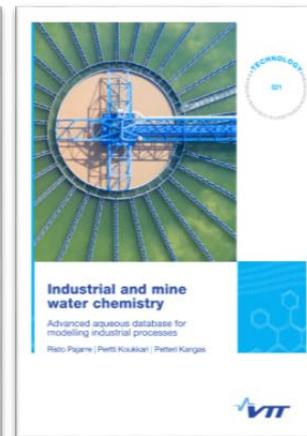
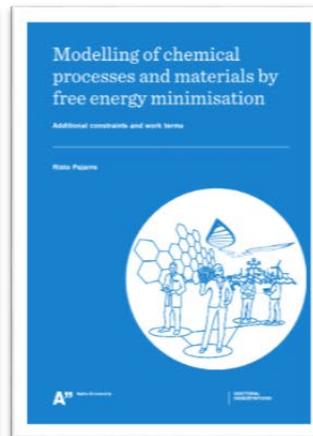
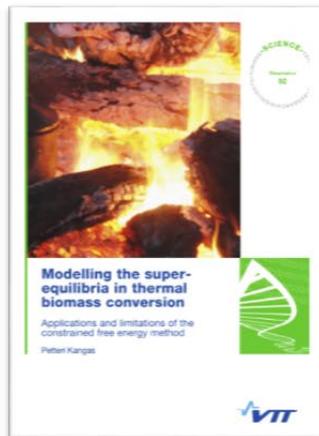
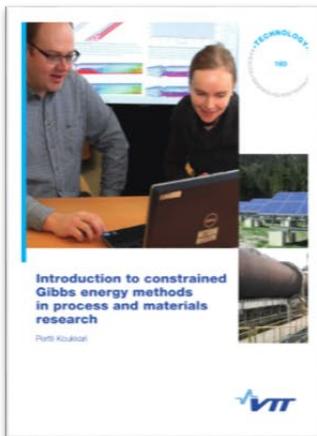
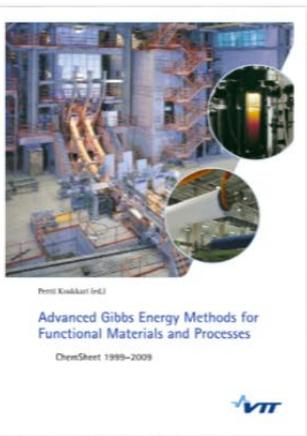
# Summary

- $D, \xi$ -technique is generally applicable in Calphadian problems\*
- Allows for graphical studies of partial equilibrium conditions (as typical phase diagrams) during the course of selected slow reactions
- $\Rightarrow$  new kinds of phase diagrams which include the driving force and extent of chemical change as axis variables
- currently implemented in FactSage in the form of virtual (massless)  $Q_{a,b,c\dots}$  components

\*Koukkari, P. , Pajarre R.: Phase diagrams with the driving force and extent of reaction as axis variables, Calphad Journal (in press).



# More details & references



Thank you for your attention!

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