Constrained and generalized Free energy models using ChemSheet

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Outline

- Introduction / Theory
- Application examples
    - Constrained reactions
    - Para-equilibrium
    - External magnetic field
    - Biochemical standard states
    - Surface energy and Nanoparticles
- Summary

Theory

- Traditional problem statement:

Find minimum of

$$G = \sum_\alpha \sum_i \mu_i^\alpha\left(x_j^\alpha, T, P\right) n_i^\alpha$$

Subject to constraints

$$n_i^\alpha \geq 0 \quad \forall\, i$$

and

$$\mathbf{An} - \mathbf{b} = \mathbf{0}$$

Standard state chemical potentials are assumed to be functions of temperature and pressure

$$\mu_i^0 = \mu_i^0(T, P)$$

- In the most typical case the user specifies T, P and **b**
- Target calculations with specified H,V, phase amount or precipitation or a specified μ_i also possible

Constrained and extended models

- Additional constraints
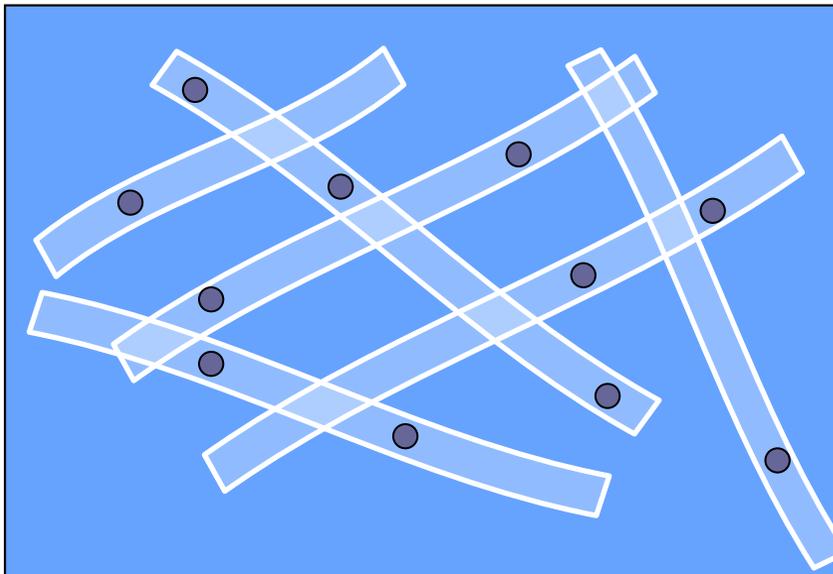 - Reaction extents, surface area, charge balances…
- Additional work terms

$$dU = TdS - pdV + \sigma dA + \phi^\alpha F z_i dn_i^\alpha + B \cdot dm\ [+L_j dl_j]\ \dots$$

L_j : an intensive work coefficient

l_j : an extensive work coordinate

Constrained and extended models

- Additional constraints applied by defining additional components to the system

		O	H	N	Na	C	Ca	$Acid_a$	e^-	$solvent_2$	$charge_2$
Gas	N_2(g)			2							
	O_2(g)	2				1					
	CO_2(g)	2				1					
External Solution	H_2O	1	2								
	H^+		1						-1		
	OH^-	1	1						1		
	Na^+				1				-1		
	CO_2	2				1			1		
	HCO_3^-	3	1			1			1		
	CO_3^{2-}	3				1			2		
	Ca^{2+}						1		-2		
Pulp	H_2O	1	2							1	
	H^+		1						-1		1
	OH^-	1	1						1		-1
	Na^+				1				-1		1
	CO_2	2				1					
	HCO_3^-	3	1			1			1		-1
	CO_3^{2-}	3				1			2		-2
	Ca^{2+}						1		-2		2
	$AcidH_a$		1					1			
	$Acid_a^-$							1	1		-1
	$CaCO_3$	3				1	1				

Constrained and extended models

- Additional work terms
  - Defining a additional component with a fixed amount is analogous to new work term with a fixed extensive work coordinate (l_j)
  - In equilibrium

$$G = \sum_i \mu_i n_i = \sum_k \pi_k b_k$$

$$\mu_i = \sum_k a_{k,i} \pi_k$$

Constrained and extended models

$$b_j \propto l_j$$

Here $l_j = V^{(2)}$ or $q^{(2)}$

$$\pi_j \propto L_j$$

Here $L_j = \Delta P$ or $\Delta \phi$

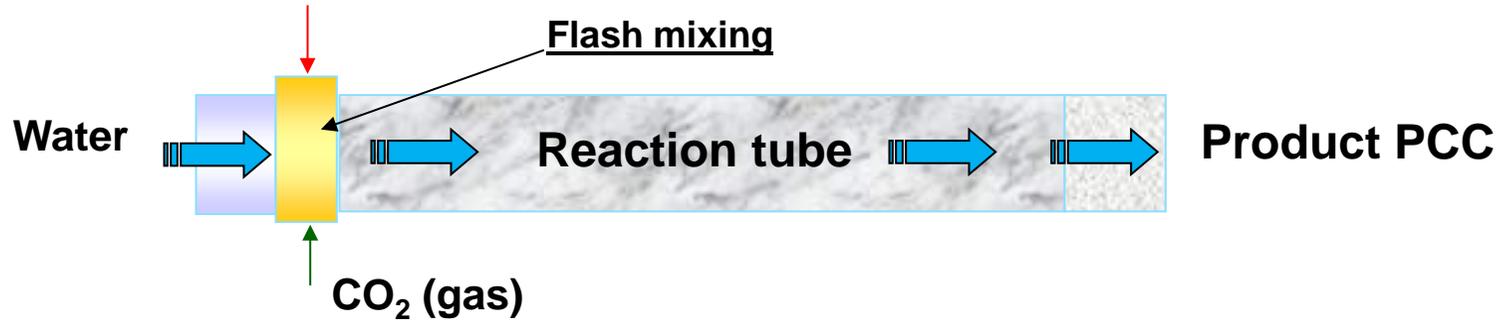|		O	H	N	Na	C	Ca	$Acid_a$	e^-	$solvent_2$	$charge_2$
Gas	$N_2(g)$			2							
	$O_2(g)$	2									
	$CO_2(g)$	2				1					
External Solution	H_2O	1	2								
	H^+		1						-1		
	OH^-	1	1						1		
	Na^+				1				-1		
	CO_2	2				1			1		
	HCO_3^-	3	1			1			1		
	CO_3^{2-}	3				1			2		
	Ca^{2+}						1		-2		
Pulp	H_2O	1	2							1	
	H^+		1						-1		1
	OH^-	1	1						1		-1
	Na^+				1				-1		1
	CO_2	2				1					
	HCO_3^-	3	1			1			1		-1
	CO_3^{2-}	3				1			2		-2
	Ca^{2+}						1		-2		2
	$AcidH_a$		1					1			
	$Acid_a^-$							1	1		-1
	$CaCO_3$	3				1	1				

Constrained and extended models

- New work terms with a fixed intensive work coefficient (such as external magnetic field) can be applied by either redefining the standard state chemical potentials or by defining a new related component with a fixed chemical potential (the latter option may be more flexible)
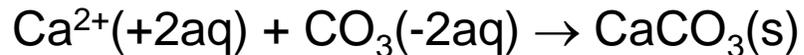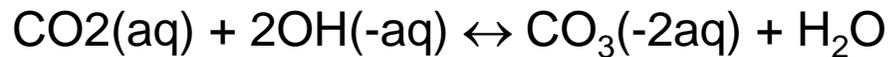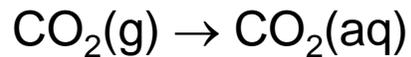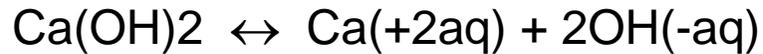
Constrained reaction extent

- New component s are defined for the system stoichiometry
- Changing the amount of a component changes the extent of the corresponding reaction

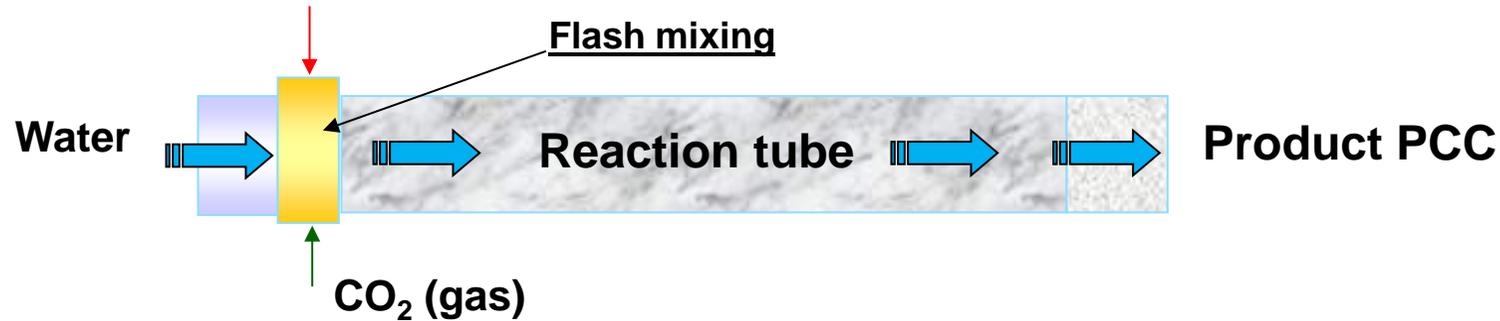$$db_R = \sum_i a_{R,i} dn_i \equiv d\xi_R$$

Restricted reactions: CaCO₃ precipitation

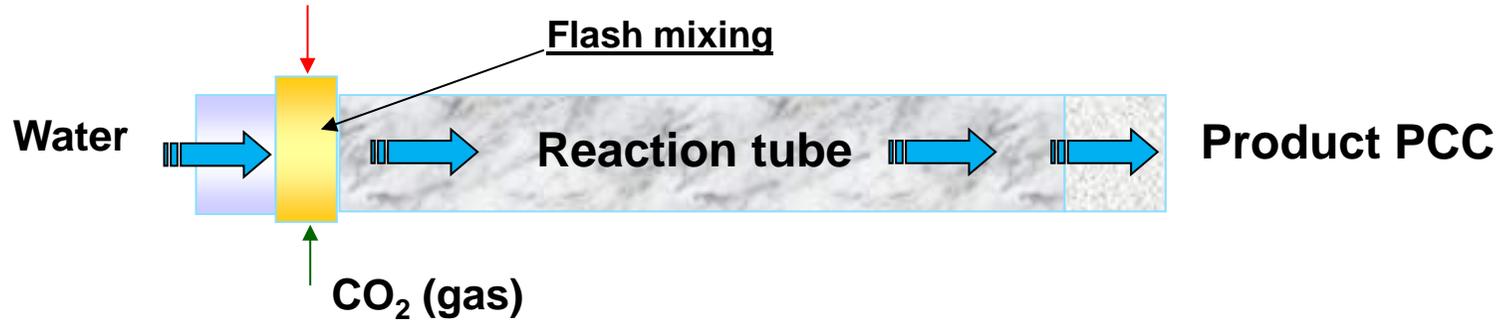**Flash mixing**

Water → Reaction tube → Product PCC

CO₂ (gas)

Reactions

$Ca(OH)2 \leftrightarrow Ca(+2aq) + 2OH(-aq)$

$CO_2(g) \rightarrow CO_2(aq)$

$CO2(aq) + 2OH(-aq) \leftrightarrow CO_3(-2aq) + H_2O$

$Ca^{2+}(+2aq) + CO_3(-2aq) \rightarrow CaCO_3(s)$

Restricted reactions: CaCO₃ precipitation

		C	H	Ca	O	e-
g	H2O(g)		2		1	
	CO2(g)	1			2	
	O2(g)				2	
aq	H2O		2		1	
	H(+aq)		1			-1
	OH(-aq)		1		1	1
	CO2(aq)	1			2	
	HCO3(-aq)	1	1		3	1
	CO3(-2aq)	1			3	2
	Ca(+2aq)			1		-2
	CaCO3(aq)	1		1	3	
CaCO3	CaCO3	1		1	3	

Restricted reactions: $CaCO_3$ precipitation

Flash mixing

Water → Reaction tube → Product PCC

CO_2 (gas)

Reactions

$Ca(OH)2 \leftrightarrow Ca(+2aq) + 2OH(-aq)$

$CO_2(g) \rightarrow CO_2(aq)$

$CO2(aq) + 2OH(-aq) \leftrightarrow CO_3(-2aq) + H_2O$

$Ca^{2+}(+2aq) + CO_3(-2aq) \rightarrow CaCO_3(s)$
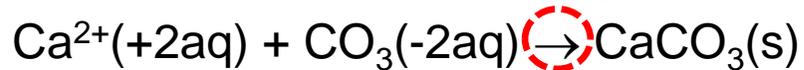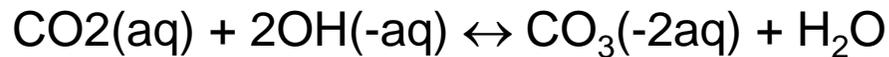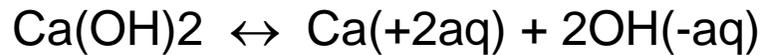
Restricted reaction example

(Reactant)

(Product)

Mönchengladbach

Herzogerath

Aachen Hbf

Cologne

Restricted reaction

- For a multicomponent system, where also a number of equilibrium reactions are possible having a one or more constrained reaction means
  - The amount of reactants is fixed

  or

  - The amount of products is fixed

  or more generally

  - There exist some (any) other linear relationship between the allowed amounts of species in the system that one could not deduce from the regular mass balance relationships alone

$$db_R = \sum_i a_{R,i} dn_i \equiv d\xi_R$$

CaCO$_3$ precipitation

		C	H	Ca	O	e-
g	H2O(g)		2		1	
	CO2(g)	1			2	
	O2(g)				2	
aq	H2O		2		1	
	H(+aq)		1			-1
	OH(-aq)		1		1	1
	CO2(aq)	1			2	
	HCO3(-aq)	1	1		3	1
	CO3(-2aq)	1			3	2
	Ca(+2aq)			1		-2
	CaCO3(aq)	1		1	3	
CaCO3	CaCO3	1		1	3	

CaCO$_3$ precipitation

		C	H	Ca	O	e-	R(CO2)	R(CaCO3)
g	H2O(g)		2		1			
	CO2(g)	1			2		1	
	O2(g)				2			
aq	H2O		2		1			
	H(+aq)		1			-1		
	OH(-aq)		1		1	1		
	CO2(aq)	1			2			
	HCO3(-aq)	1	1		3	1		
	CO3(-2aq)	1			3	2		
	Ca(+2aq)			1		-2		
	CaCO3(aq)	1		1	3			
CaCO3	CaCO3	1		1	3			1

CaCO$_3$ precipitation

		C	H	Ca	O	e-	R(CO2)	R(CaCO3)
g	H2O(g)		2		1			
	CO2(g)	1			2		1	
	O2(g)				2			
aq	H2O		2		1			
	H(+aq)		1			-1		
	OH(-aq)		1		1	1		
	CO2(aq)	1			2			
	HCO3(-aq)	1	1		3	1		
	CO3(-2aq)	1			3	2		
	Ca(+2aq)			1		-2		
	CaCO3(aq)	1		1	3			
CaCO3	CaCO3	1		1	3			1
R(CO2)+	R(CO2)+						1	
R(CO2)-	R(CO2)-						-1	
R(CaCO3)+	R(CaCO3)+							1
R(CaCO3)-	R(CaCO3)-							-1

CaCO$_3$ precipitation
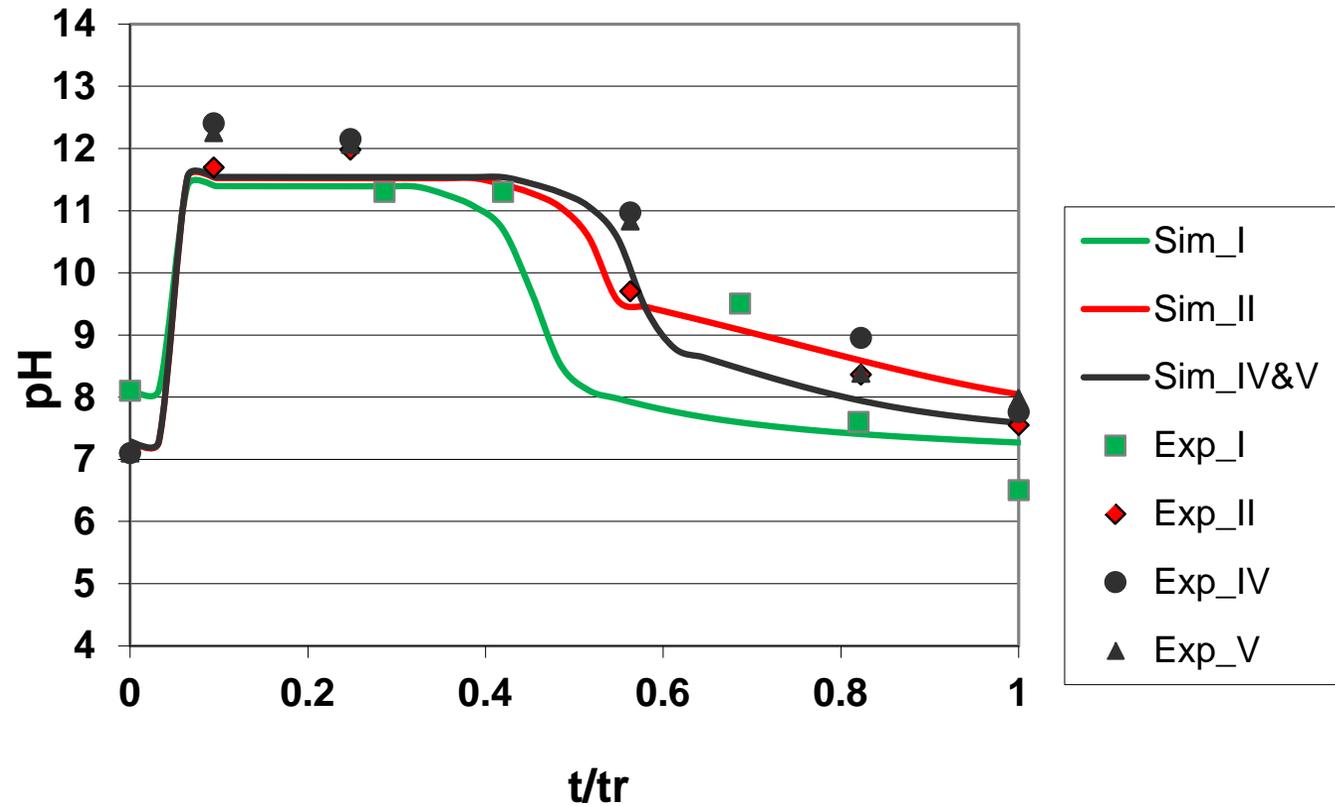
Paraequilibrium

- From modelling perspective chemical reactions and mass transfer between phases are basically identical processes, in both one or more phase constituents in system are transformed to different constituents, subject to (normal) mass balance constraints

- In rapidly cooling systems a para- equilibrium state may result in which rapidly diffusing elements have reached equilibrium but more slowly diffusing elements have remained essentially immobile. This means that the for any new phases the relative amounts of immobile components must be the same as in the parent phase

- Ratio of iron to alloying metal Me in a new phase α is the same as in the parent phase, so for any changes in system composition:

$$\frac{db_{Fe}^{\alpha}}{db_{Me}^{\alpha}} = \frac{b_{Fe}^{\alpha}}{b_{Me}^{\alpha}}$$

where $b_X^{\alpha} = \sum_i a_{X,i} n_i^{\alpha}$

- This can be rearranged to

$$b_{Fe} \sum_i \left(a_{i,Me} dn_i^{\alpha} \right) - b_{Me} \sum_i \left(a_{i,Fe} dn_i^{\alpha} \right)$$

$$= \sum_i \left(b_{Fe} a_{i,Me} - b_{Me} a_{i,Fe} \right) dn_i^{\alpha}$$

Stoichiometric coefficient

$$\sum_i \left(\frac{b_{Fe}}{b_{Me}} \, a_{i,Me} - a_{i,Fe} \right) dn_i^{\alpha}$$

Fe:Cr:Ni relative amounts 3 : 1 : 1.5

|		Cr	Fe	Ni	C	*Cr-BCC	*Ni-BCC	*Cr-Cem	*Ni-Cem	*Cr-M23C6	*Ni-M23C6	*Cr-M7C3	*Ni-M7C3
FCC	Cr	1											
	Cr:C	1			1								
	Fe		1										
	Fe:C		1		1								
	Ni			1									
	Ni:C			1	1								
BCC	Cr	1				3							
	Cr:C	1			3	3							
	Fe		1			-1	-1						
	Fe:C		1		3	-1	-1						
	Ni			1			2						
	Ni:C			1	3		2						
Cementite	Cr:C	1			1			3					
	Fe:C		1		1			-1	-1				
	Ni:C			1	1				2				
M23C6	Cr23C6	23			6					69			
	Fe3Cr20C6	20	3		6					57	-3		
	Ni3Cr20C6	20		3	6					60	6		
	Fe20Cr3C6	3	20		6					-11	-20		
	Fe23C6		23		6					-23	-23		
	Ni3Fe20C6		20	3	6					-20	-14		
	Ni20Cr3C6	3		20	6					9	40		
	Ni20Fe3C6		3	20	6					-3	37		
	Ni23C6			23	6						46		
M7C3	Cr:C	7			3							21	
	Fe:C		7		3							-7	-7
	Ni:C			7	3								14

Phase diagrams applying paraequilibrium assumption integrated to Factsage
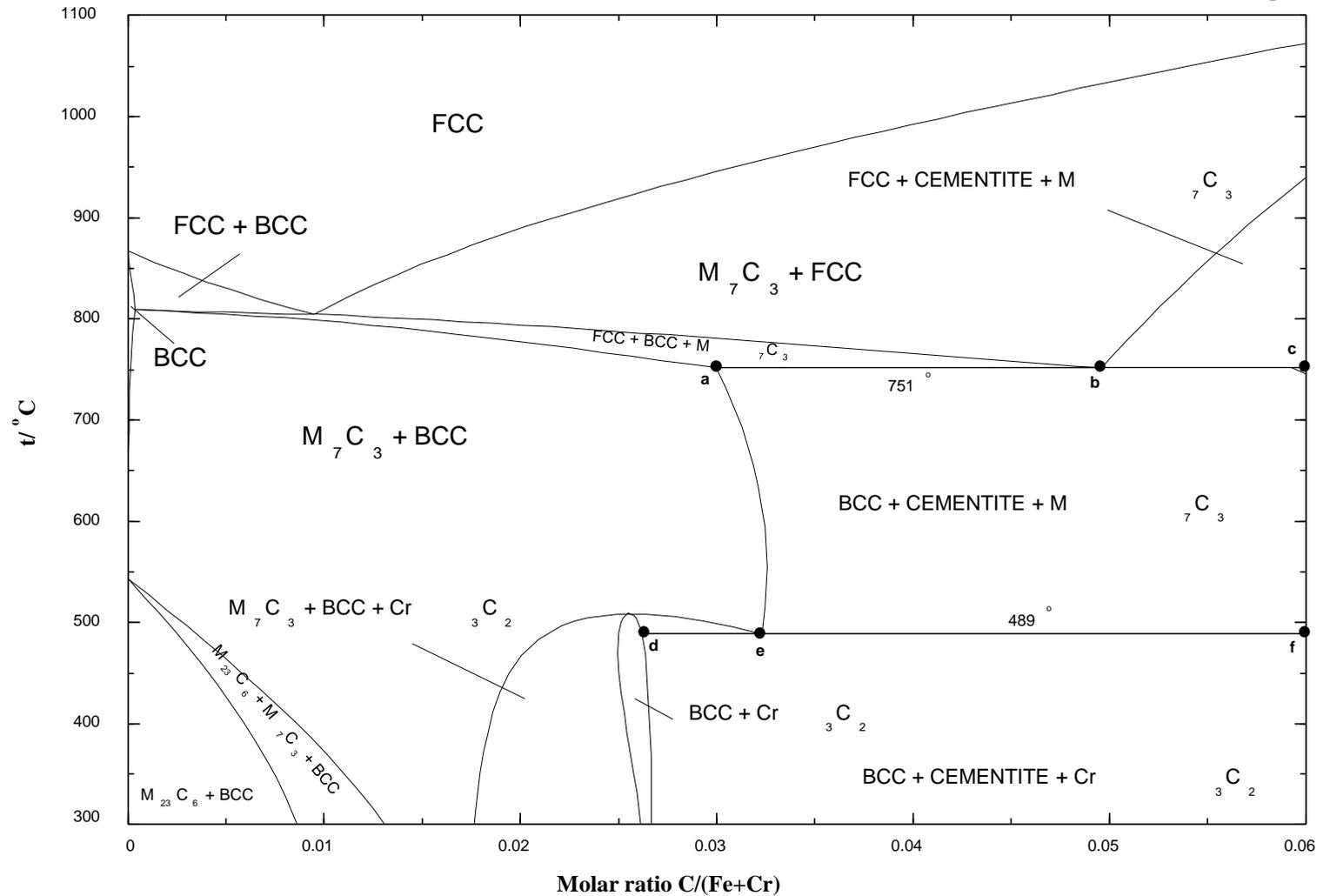
Phase diagrams applying paraequilibrium assumption integrated to Factsage

Three component system effectively becomes two component system: C : (Fe+Cr)
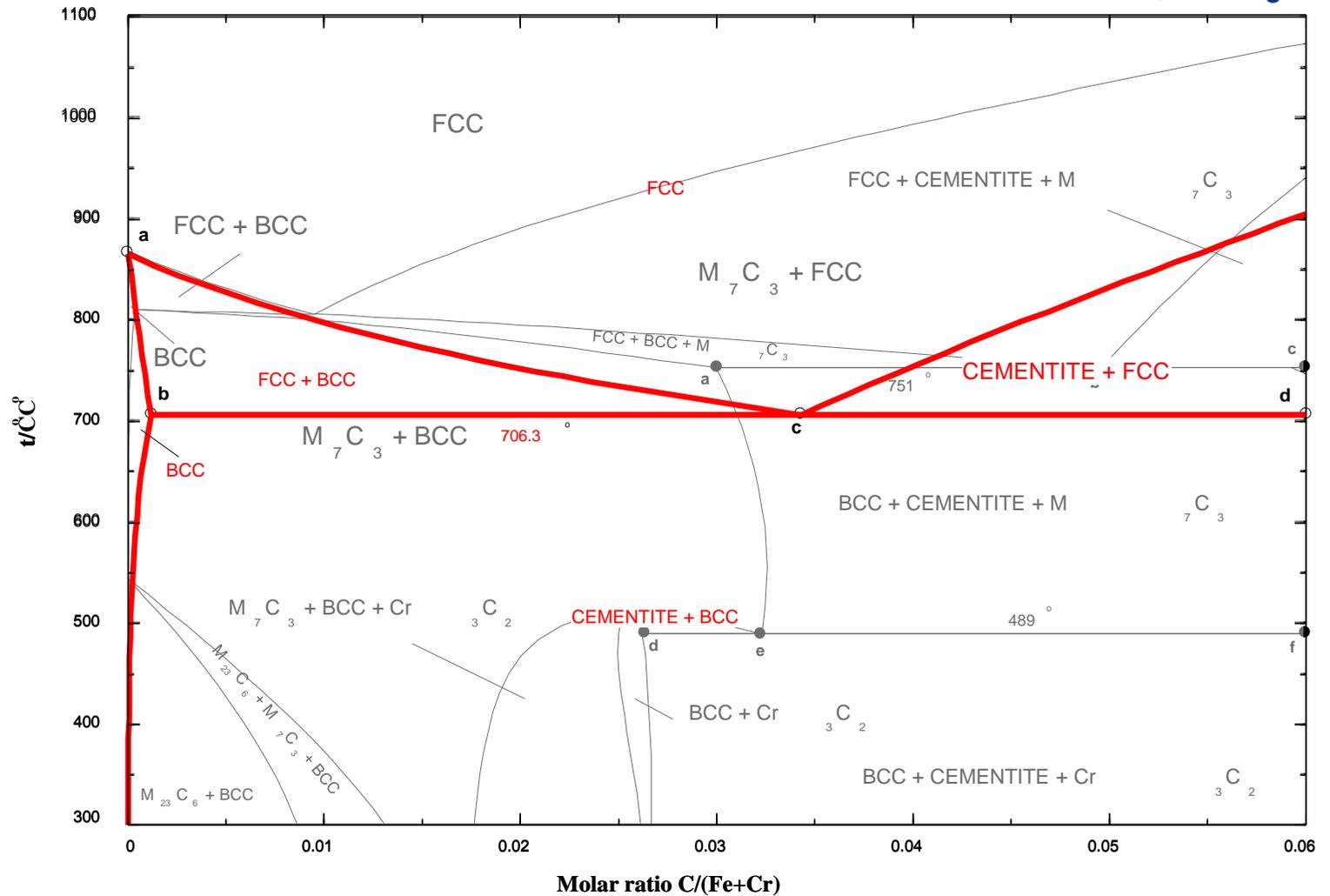
External magnetic field and magnetization

- Chemical potential with an external magnetic field present

$$\mu_i^0(T, P, B) = \mu_i^0(T, P, B = 0) - \int m_i dB$$

- Ferromagnetic material with constant magnetization

$$\mu_i^0(T, P, B) = \mu_i^0(T, P, B = 0) - m_i B$$

Paramagnetic material with magnetization proprtional to magnetic field strength

$$\mu_i^0(T, P, B) = \mu_i^0(T, P, B = 0) - 0.5\chi_i B^2$$

LaCo$_5$H$_y$ hydride

- The molar magnetic moment is increased by the amount ΔM per desorbed mole of hydrogen. Equilibrium exists between two solid hydrides and hydrogen gas

$$0.5xH_2(g) + LaCo_5H_{4.2} \leftrightarrow LaCo_5H_{4.2+x}$$

$$\Delta\mu^0 \equiv \mu^0(LaCo_5H_{4.2+X}) - \mu^0(LaCo_5H_{4.2})$$

$$\Delta\mu^0(B) = \Delta\mu^0(B = 0) + \int_0^B \Delta M dB$$

In equilibrium

$$\ln\left(\frac{P_{H_2}}{P_{H_2}^0}\right) = \frac{2}{RT}\int_0^B \Delta M dB$$

One can define a new component to the system
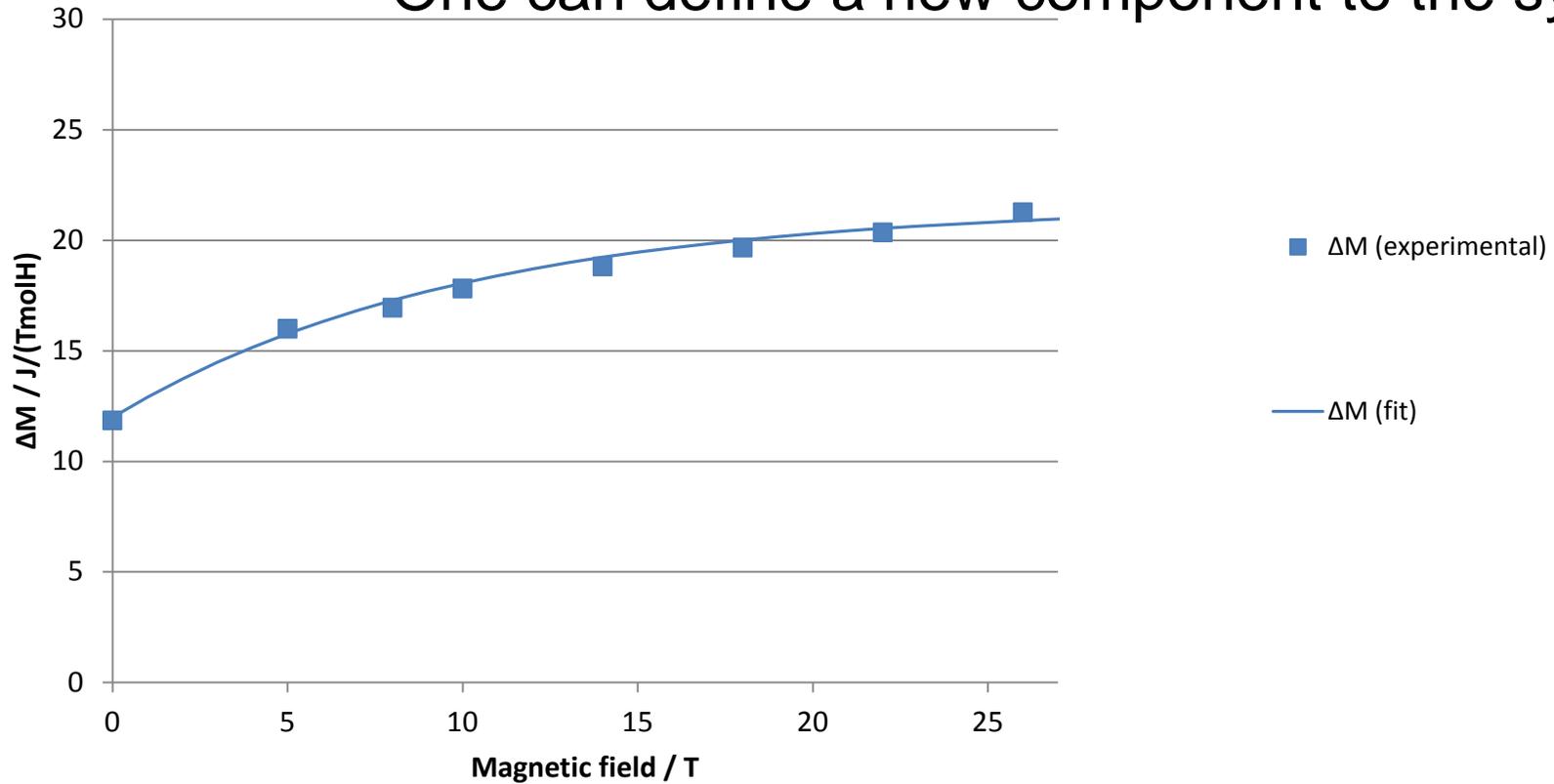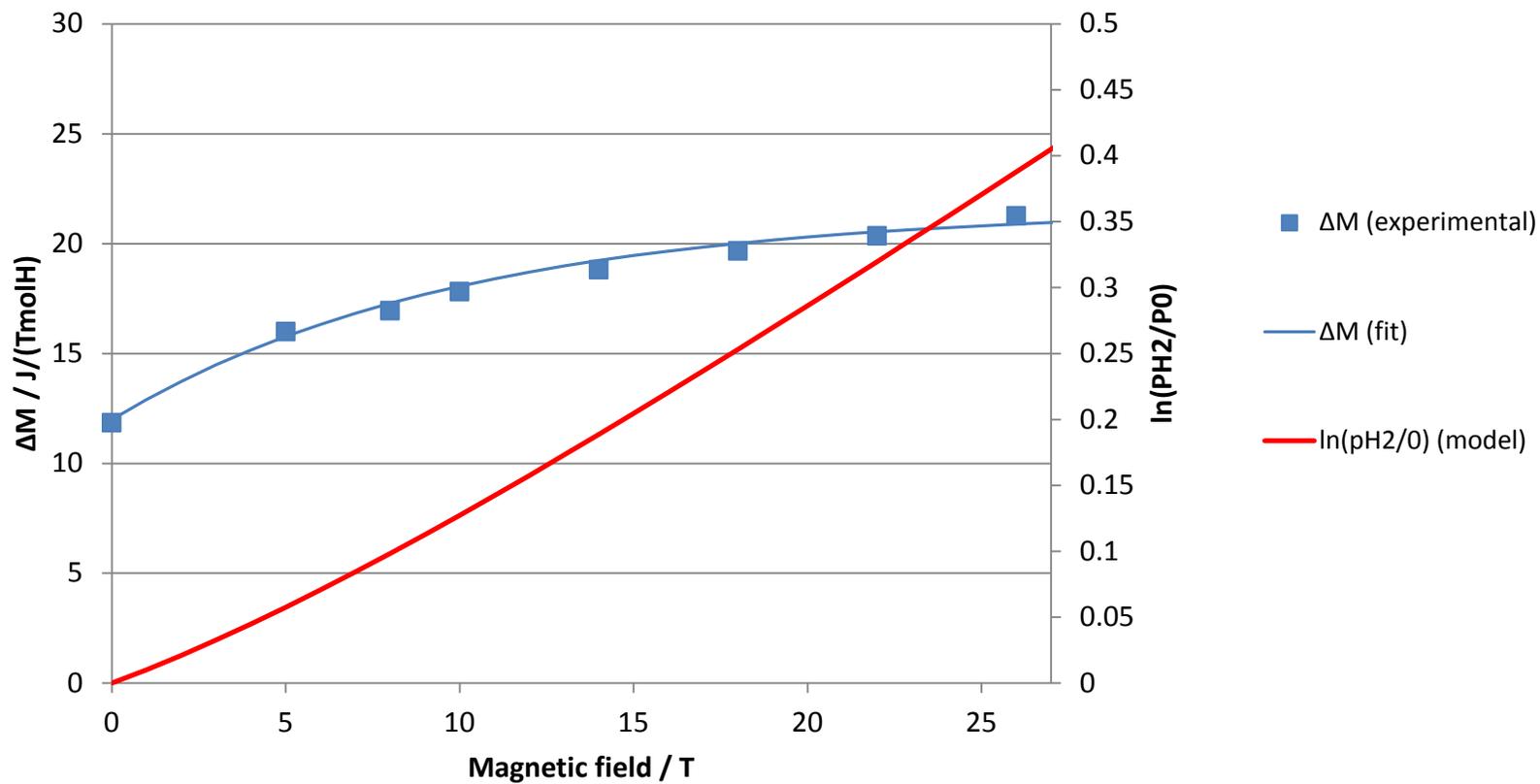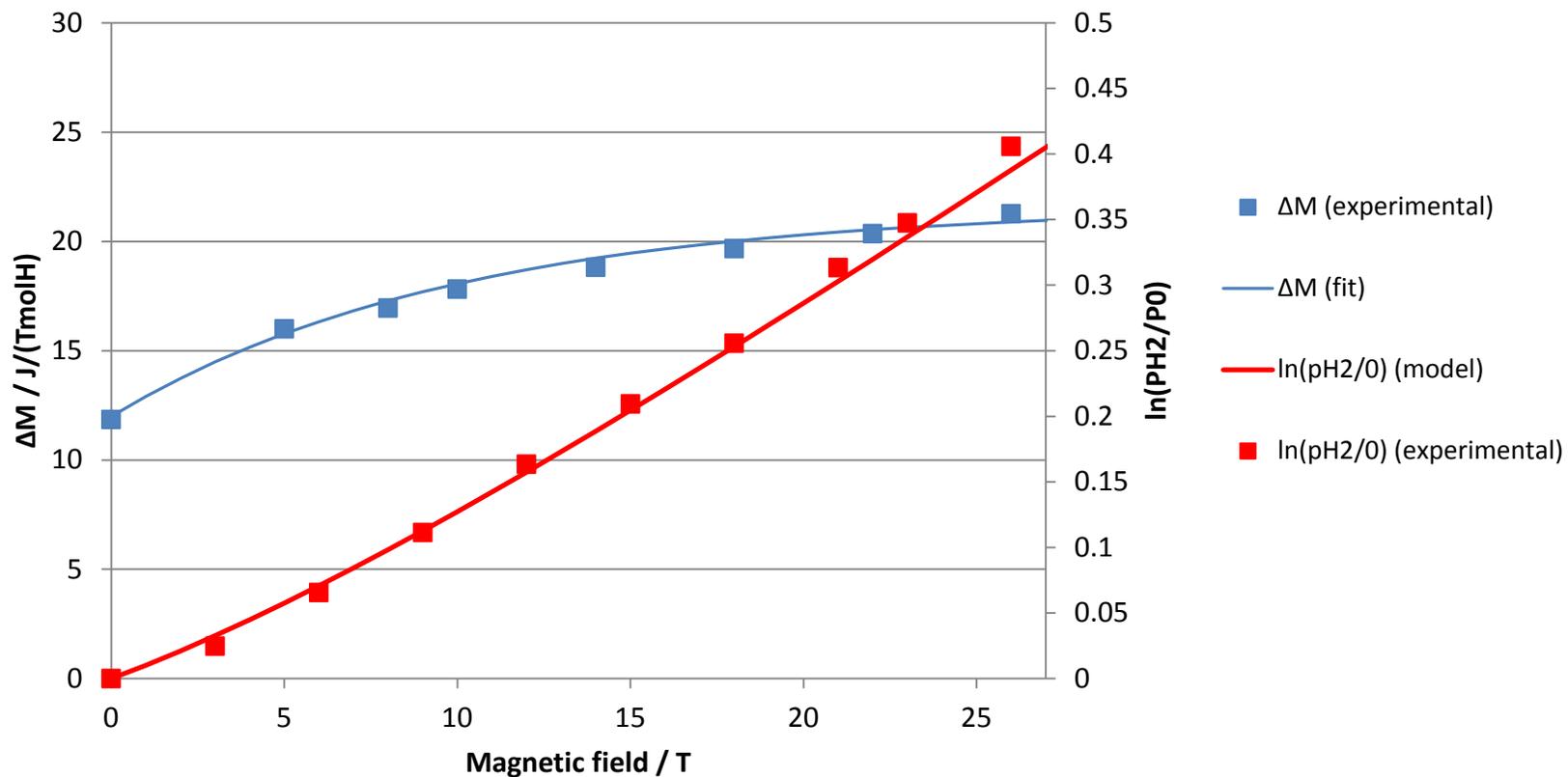
Adjusted standard states for biochemical systems

- Biochemical systems in general
    - Have a large number of species
    - It is not possible to model the interactions precisely in a thermochemical model
    - Part of the system of interest can often be considered to be connected to an infinite reservoir that keeps for example pH and some other concentrations constant
    - => There is a need for adjustments that facilitate calculations in such systems

# Adjusted standard states for biochemical systems

- For pH and other activities one can (also) use the ChemApp inbuilt target calculation option

- For generic Davies equation like adjustment to the activity coefficient with a fixed ionic strength, one can define a new component with stoichiometric coefficients equaling z_i^2 (corresponding chemical potential contribution $\frac{\alpha RT \sqrt{I}}{1+B\sqrt{I}}$
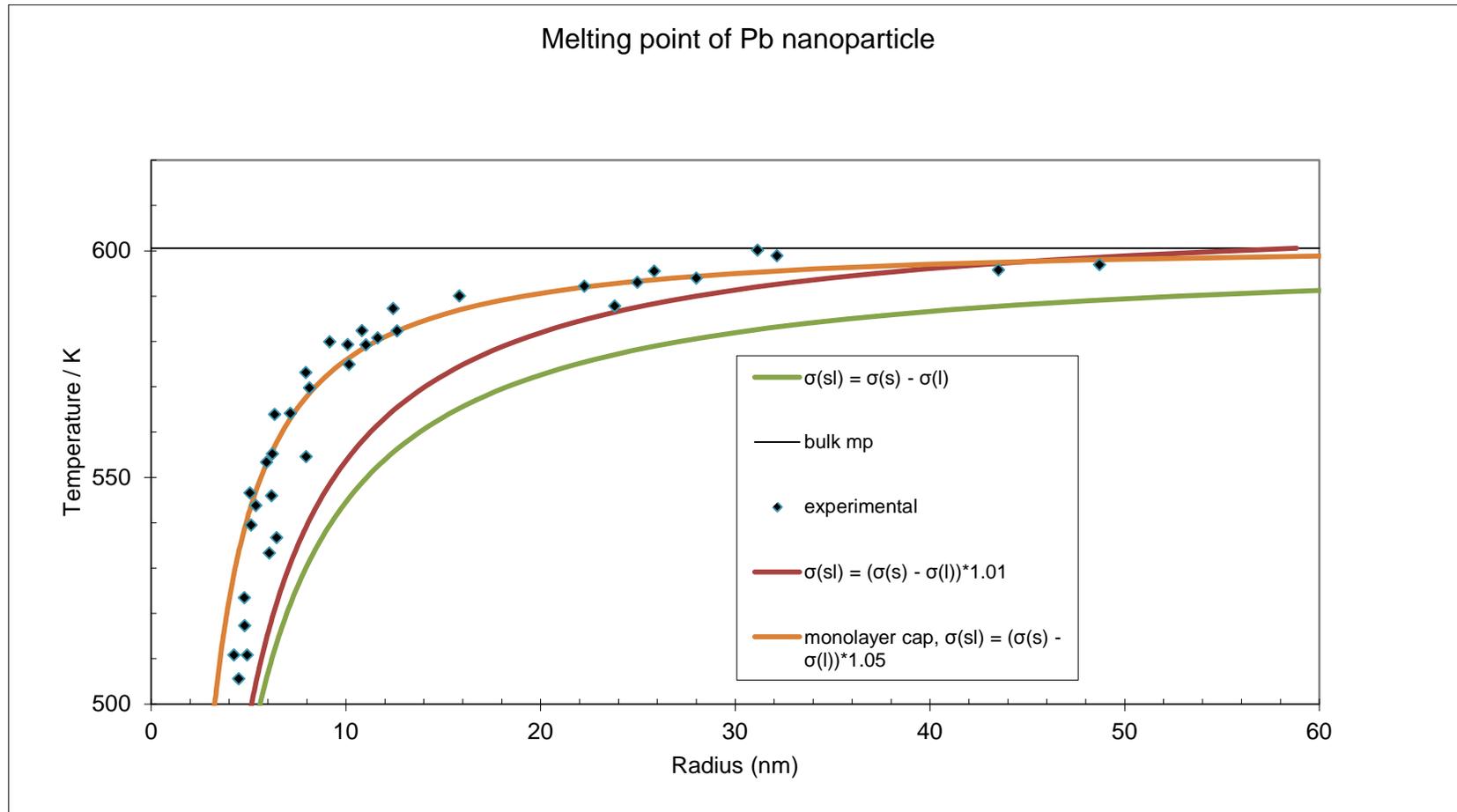
Surface energies and melting of nanoparticles
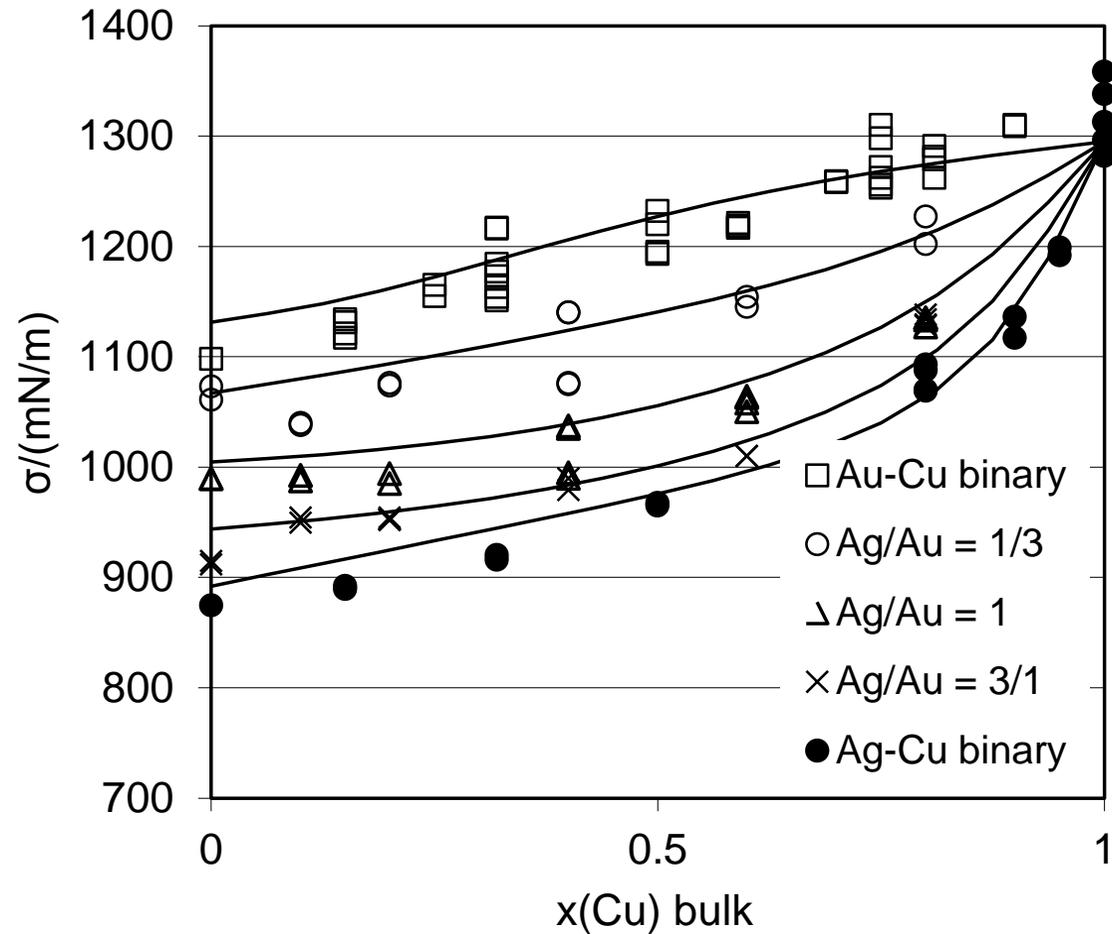
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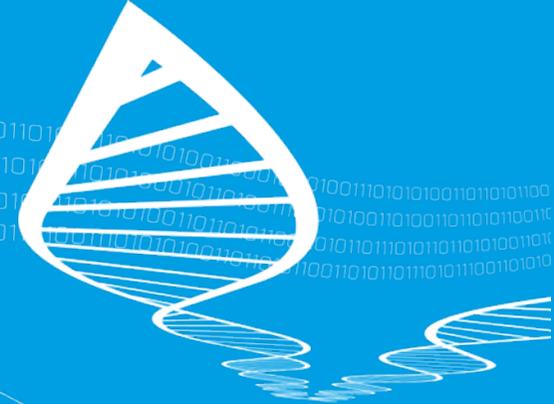

Surface tension of Fe as a function of oxygen content

Melting of nanoparticles

Melting point of Pb nanoparticle
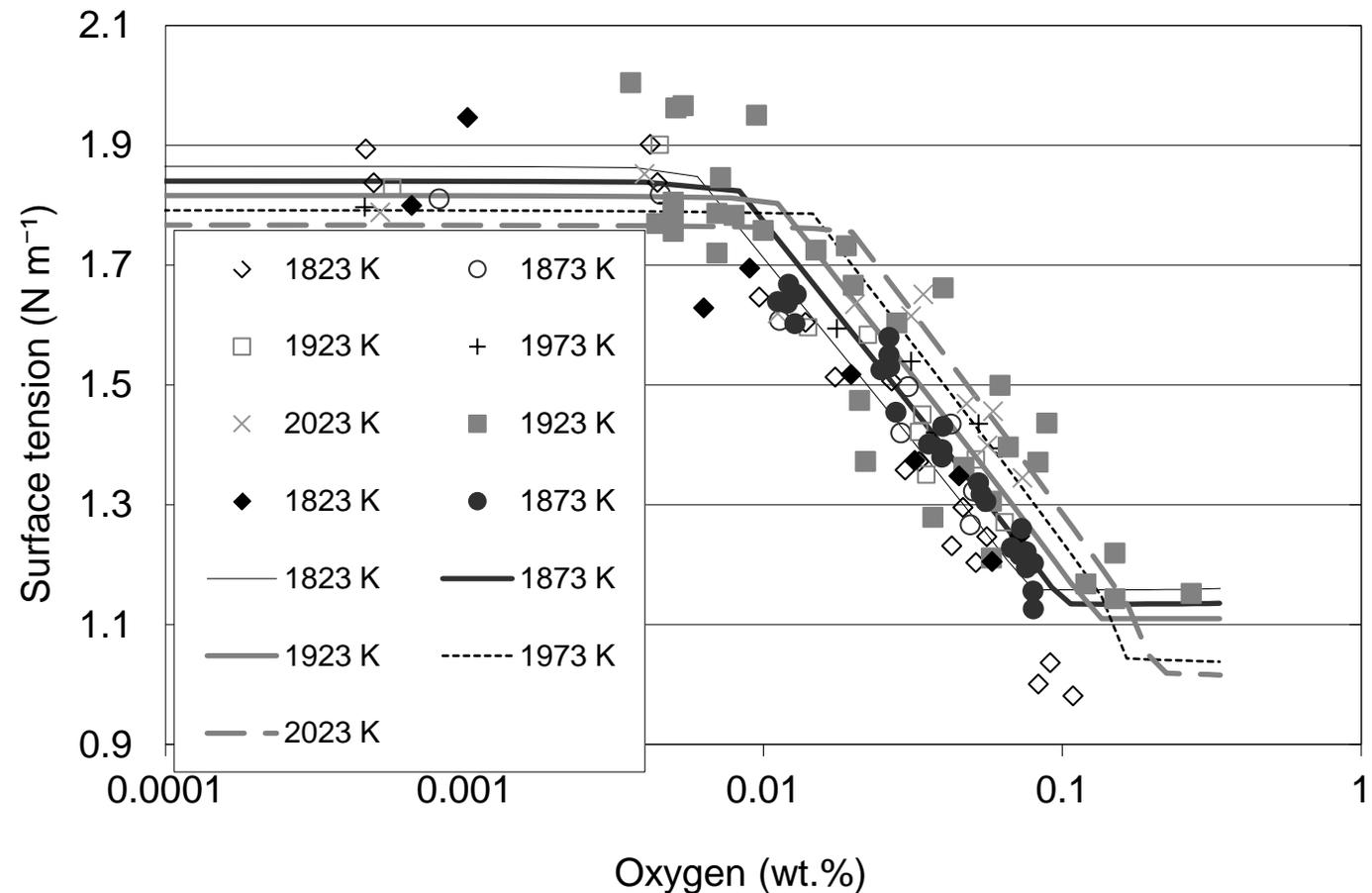
Summary

- By defining new components one can add to the system constraints either

  - to the extents of reactions taking place

  - To some other extensive variable (subvolume, area, charge) corresponding to additional work term in the free energy equation

- Or one can make adjustments to the standard states of species, corresponding to work term in external field or analogous adjustment corresponding to buffered surroundings

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