VTT TECHNICAL RESEARCH CENTRE OF FINLAND LTD

Additional constraints and work terms in Gibbs energy minimisation with ChemApp and ChemSheet

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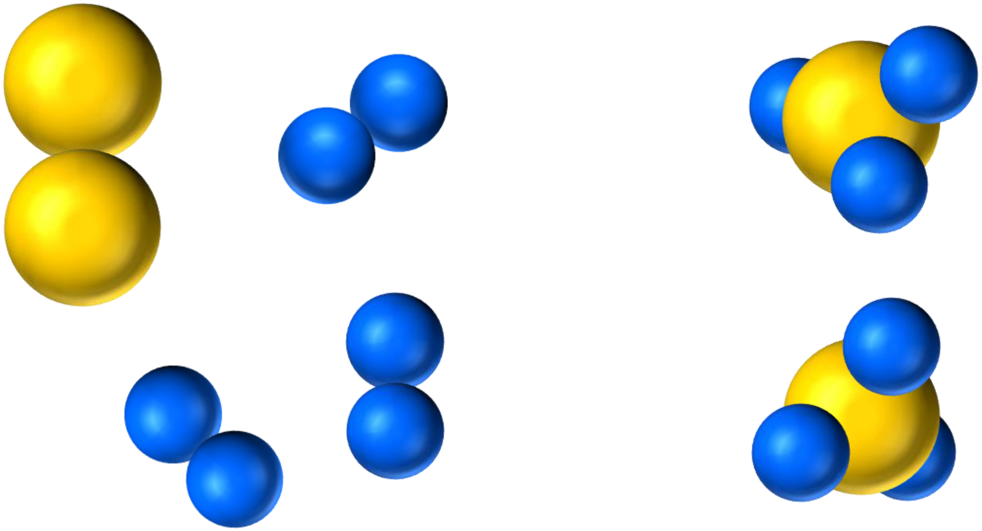
Objective: extend the applicability of min(G) solvers

- Descriptions and methods for systems in which
  - time dependency is essential:

  - or where the system is controlled by other parameters than initial amounts, temperature and pressure, such as a surface area or external fields

Time dependency: reaction equation

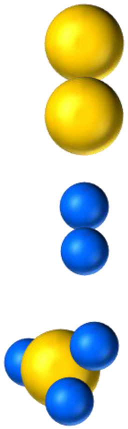


$$N_2 + 3H_2 \Leftrightarrow 2NH_3$$

Matrix description corresponding to equilibrium reaction

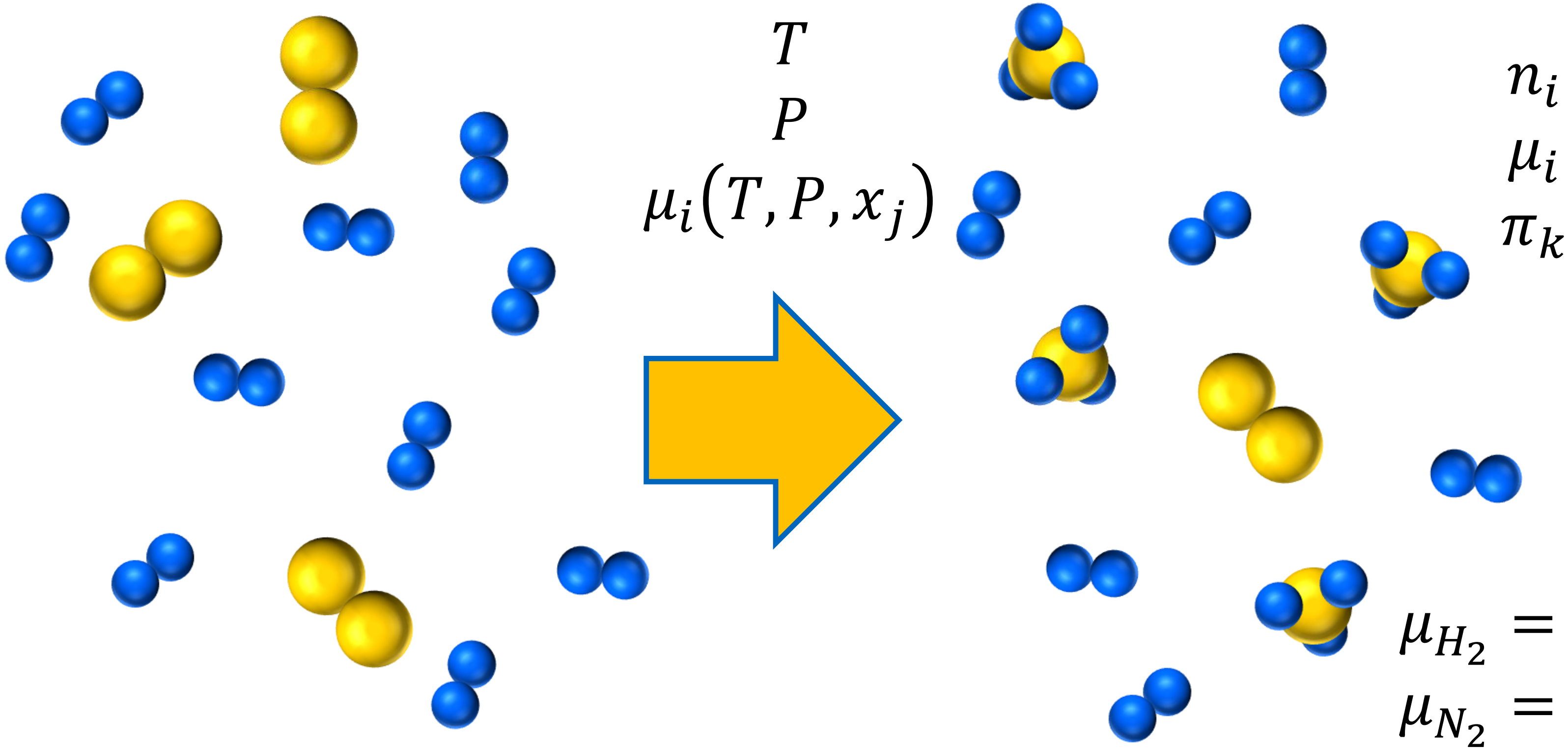
System components

Species



	N	H
N_2	2	0
H_2	0	2
NH_3	1	3

Chemical Equilibrium



T

P

$\mu_i(T, P, x_j)$

n_i

μ_i

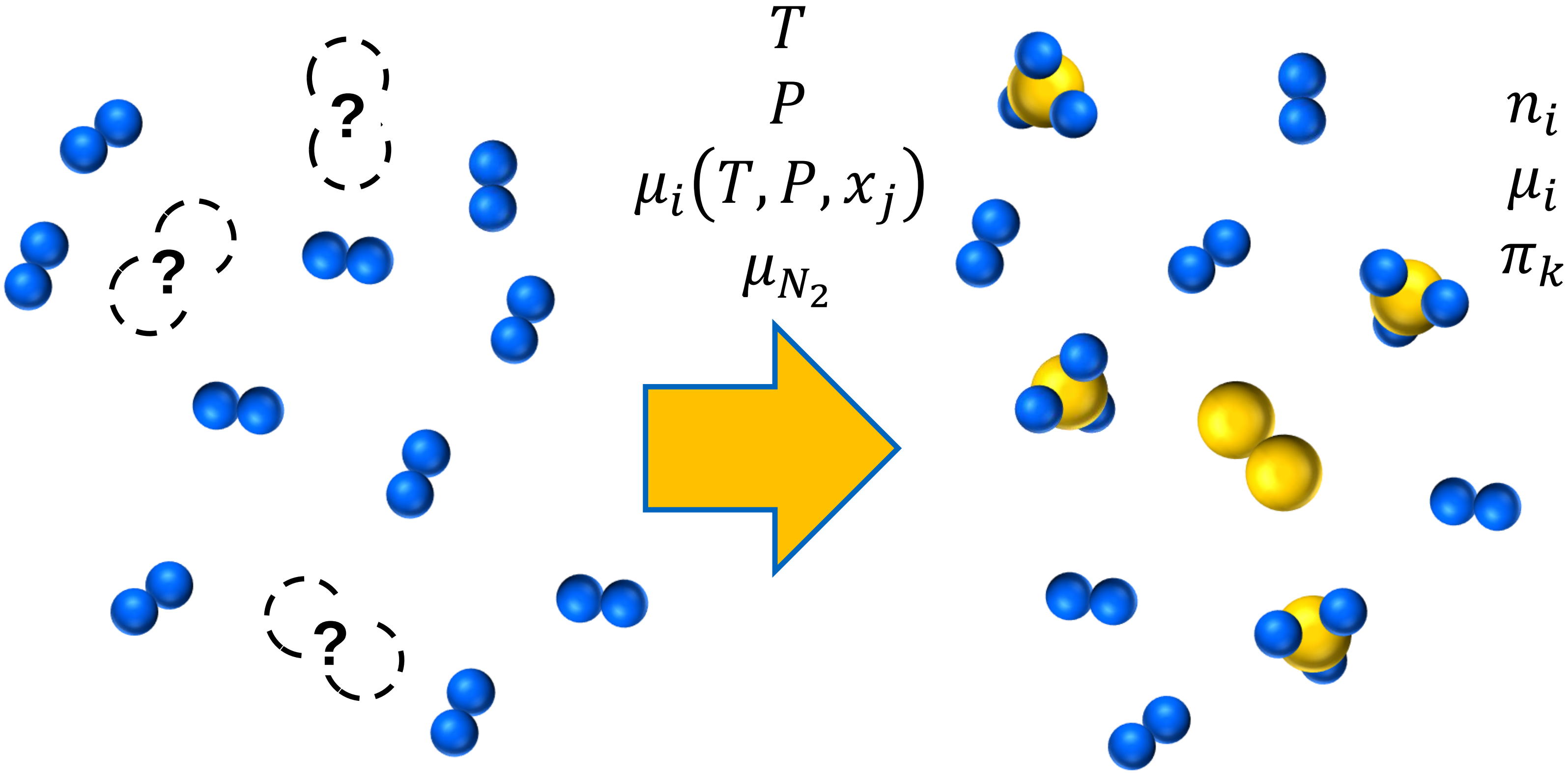
π_k

$$\mu_{H_2} = 2 \cdot \pi_H$$

$$\mu_{N_2} = 2 \cdot \pi_N$$

$$\mu_{NH_3} = \pi_N + 3\pi_3$$

Chemical equilibrium (set equilibrium μ_i)



T

P

$\mu_i(T, P, x_j)$

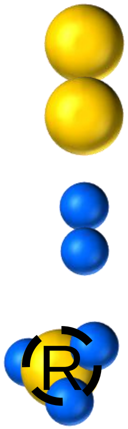
μ_{N_2}

n_i

μ_i

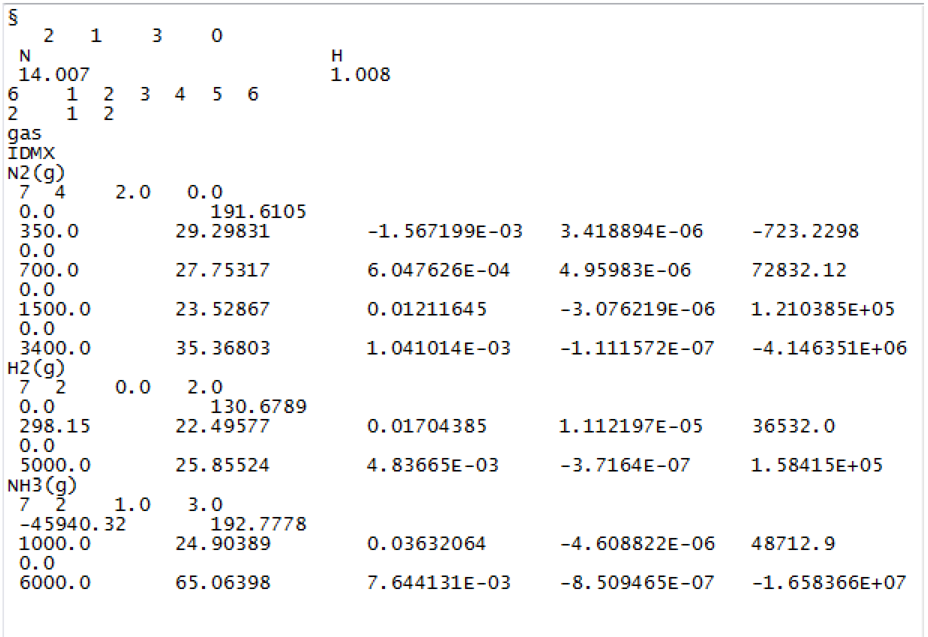
π_k

Restricting the extent of reactions

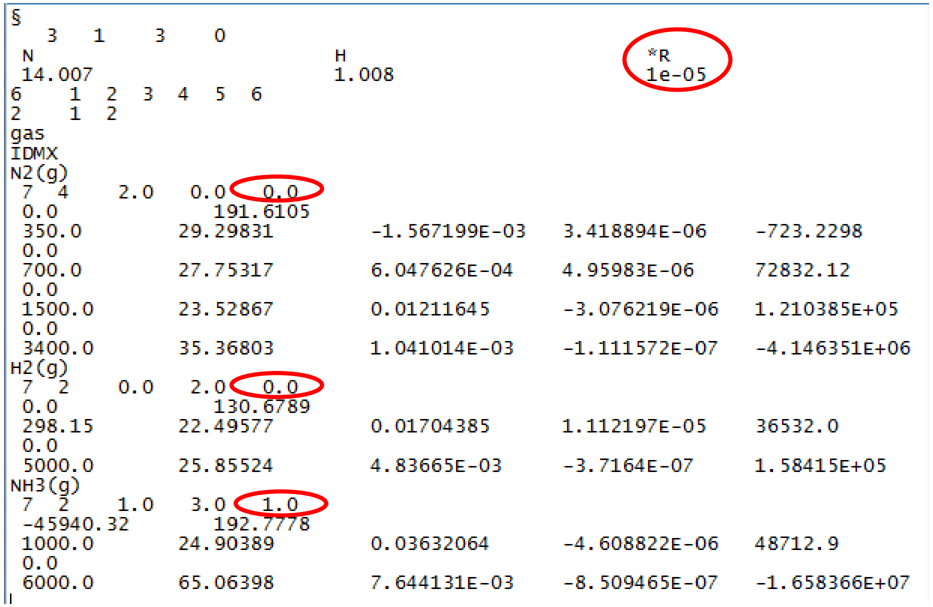


	N	H	R
N_2	2	0	0
H_2	0	2	0
NH_3	1	3	1

Restricting the extent of reactions



```
§
   2   1    3    0
 N                        H
 14.007                   1.008
6    1   2   3   4   5   6
2    1   2
gas
IDMX
N2(g)
 7  4     2.0    0.0
 0.0              191.6105
 350.0         29.29831        -1.567199E-03    3.418894E-06     -723.2298
 0.0
 700.0         27.75317        6.047626E-04     4.95983E-06      72832.12
 0.0
 1500.0        23.52867        0.01211645       -3.076219E-06    1.210385E+05
 0.0
 3400.0        35.36803        1.041014E-03     -1.111572E-07    -4.146351E+06
H2(g)
 7  2     0.0    2.0
 0.0              130.6789
 298.15        22.49577        0.01704385       1.112197E-05     36532.0
 0.0
 5000.0        25.85524        4.83665E-03      -3.7164E-07      1.58415E+05
NH3(g)
 7  2     1.0    3.0
 -45940.32        192.7778
 1000.0        24.90389        0.03632064       -4.608822E-06    48712.9
 0.0
 6000.0        65.06398        7.644131E-03     -8.509465E-07    -1.658366E+07
```



```
§
   3   1    3    0
 N                        H                          *R
 14.007                   1.008                      1e-05
6    1   2   3   4   5   6
2    1   2
gas
IDMX
N2(g)
 7  4     2.0    0.0    0.0
 0.0              191.6105
 350.0         29.29831        -1.567199E-03    3.418894E-06     -723.2298
 0.0
 700.0         27.75317        6.047626E-04     4.95983E-06      72832.12
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H2(g)
 7  2     0.0    2.0    0.0
 0.0              130.6789
 298.15        22.49577        0.01704385       1.112197E-05     36532.0
 0.0
 5000.0        25.85524        4.83665E-03      -3.7164E-07      1.58415E+05
NH3(g)
 7  2     1.0    3.0    1.0
 -45940.32        192.7778
 1000.0        24.90389        0.03632064       -4.608822E-06    48712.9
 0.0
 6000.0        65.06398        7.644131E-03     -8.509465E-07    -1.658366E+07
```
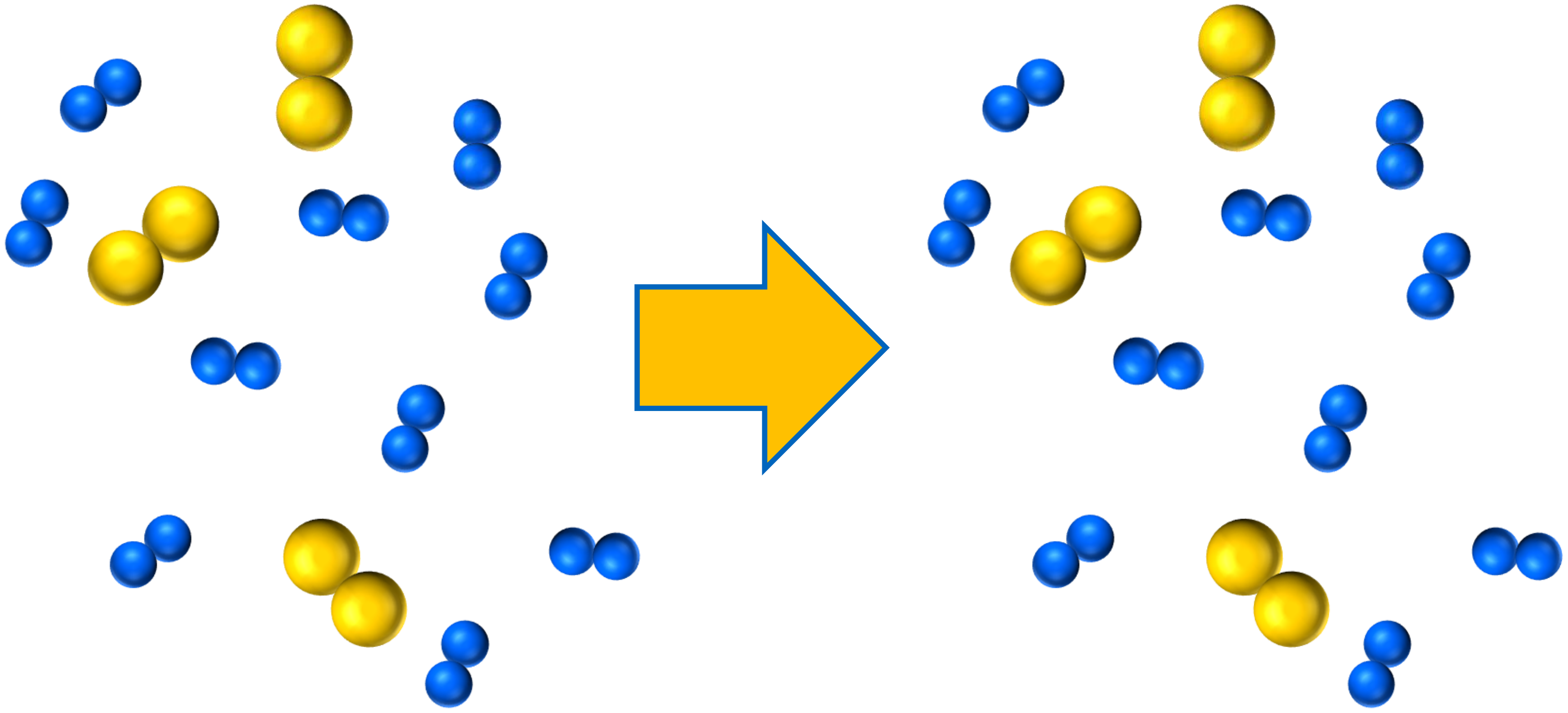
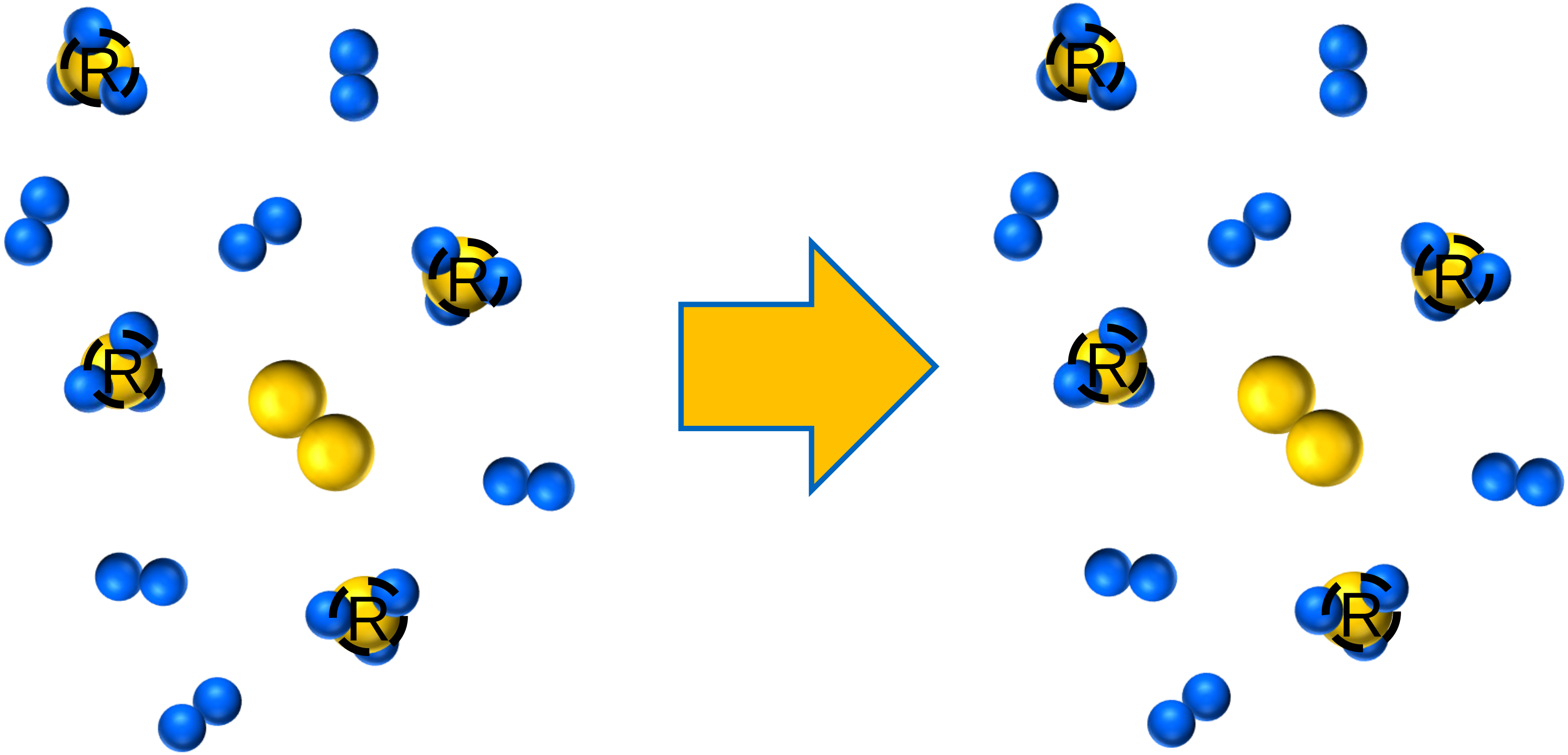

Restricting the extent of reactions

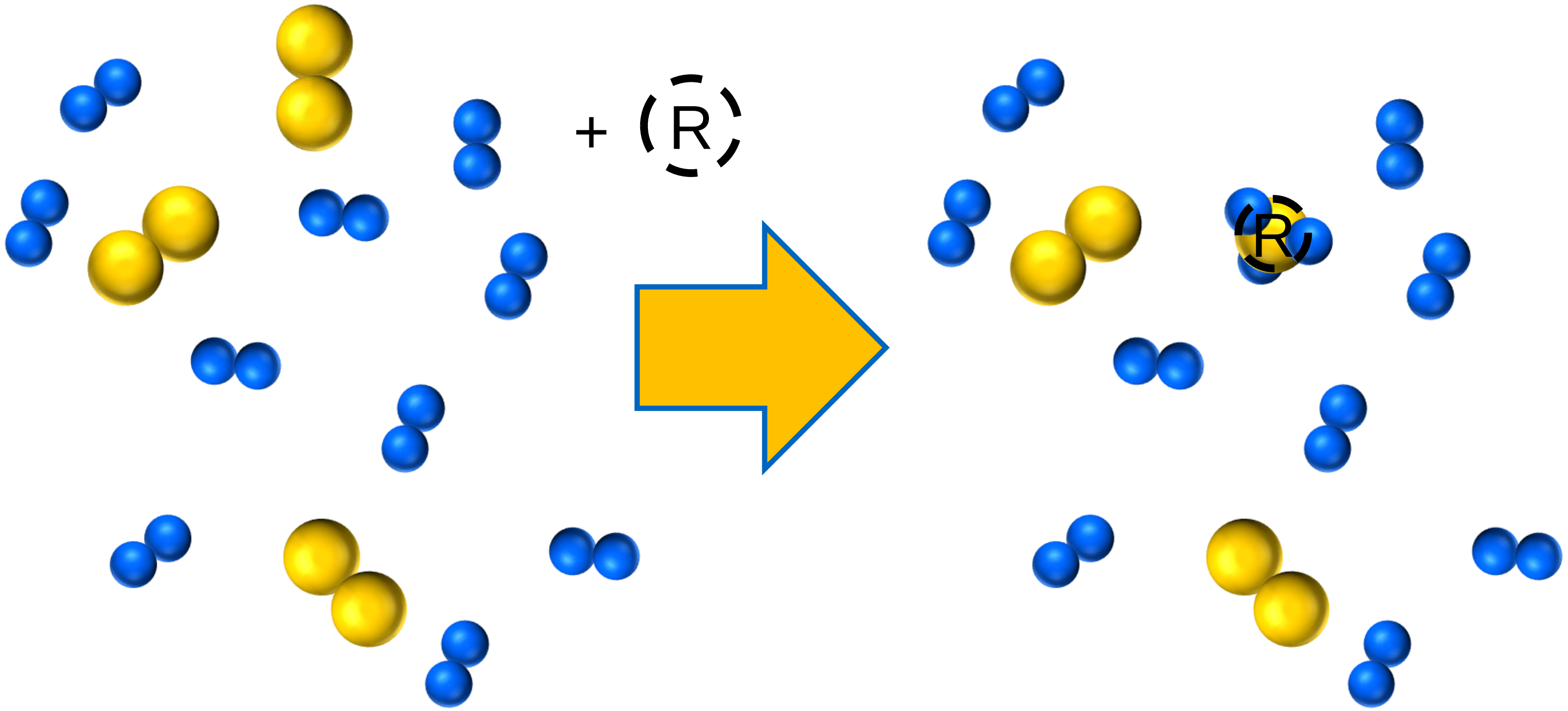


(here the final state is the same as initial state)

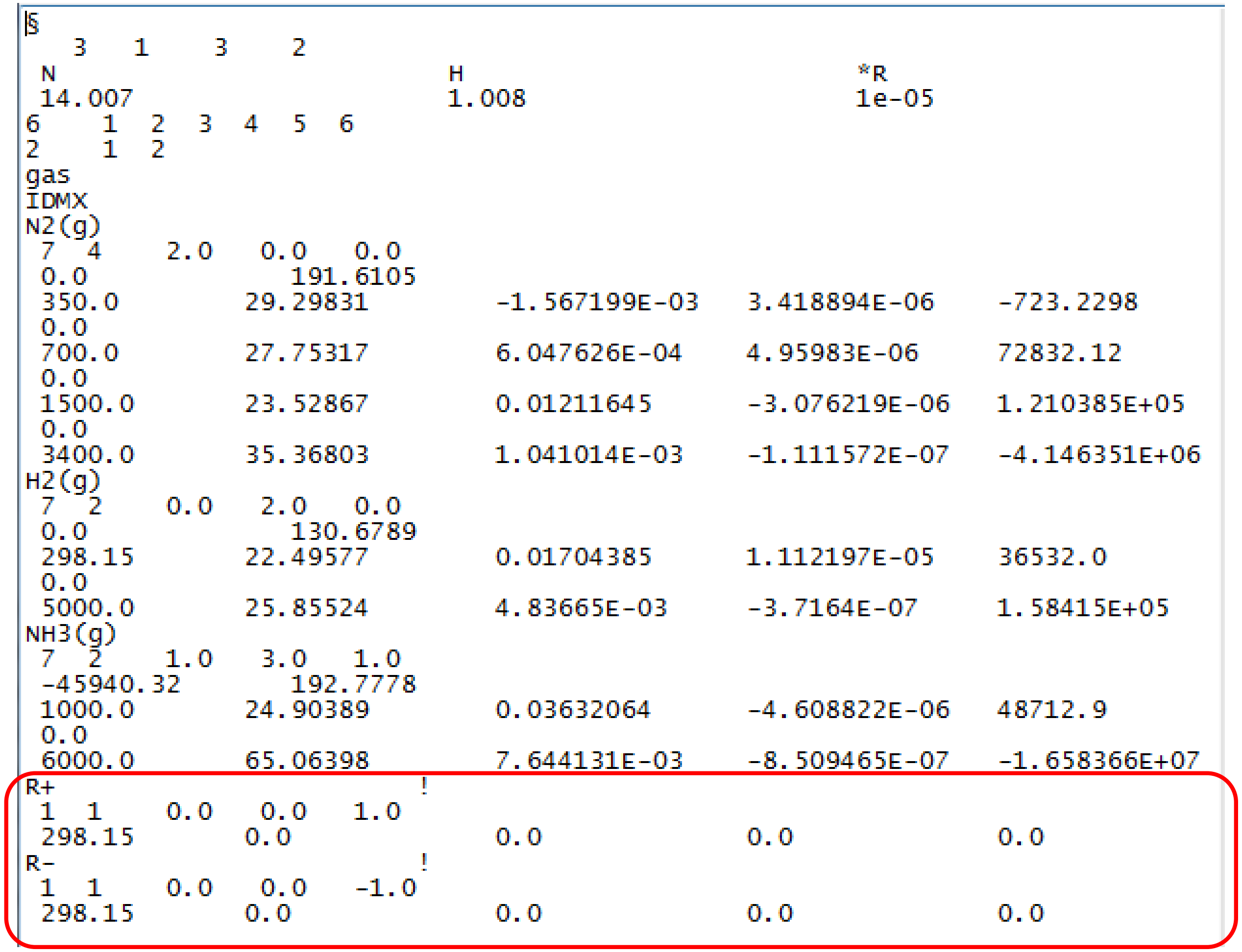
Restricting the extent of reactions



Controlling the extent of a reaction



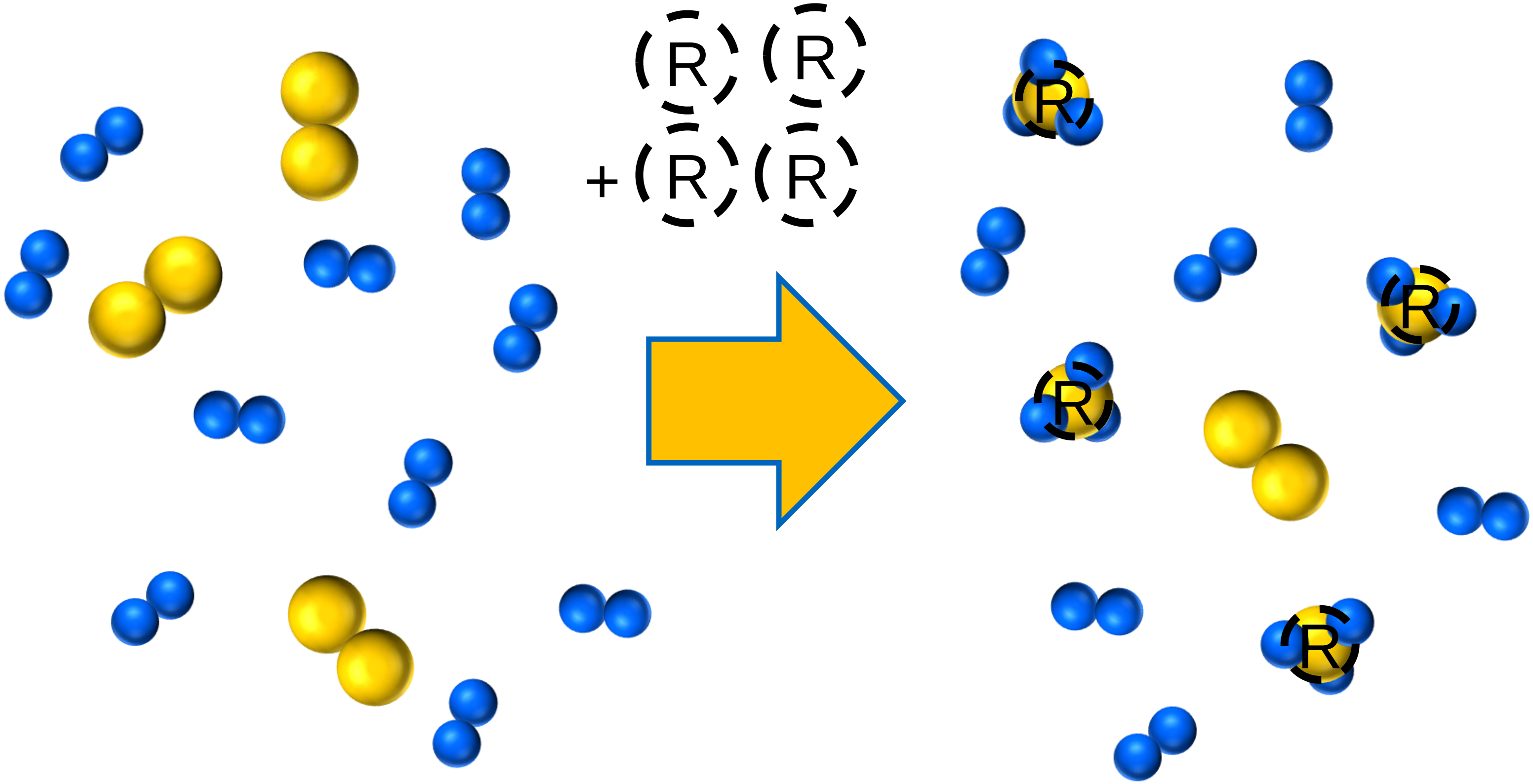
Controlling the extent of a reaction



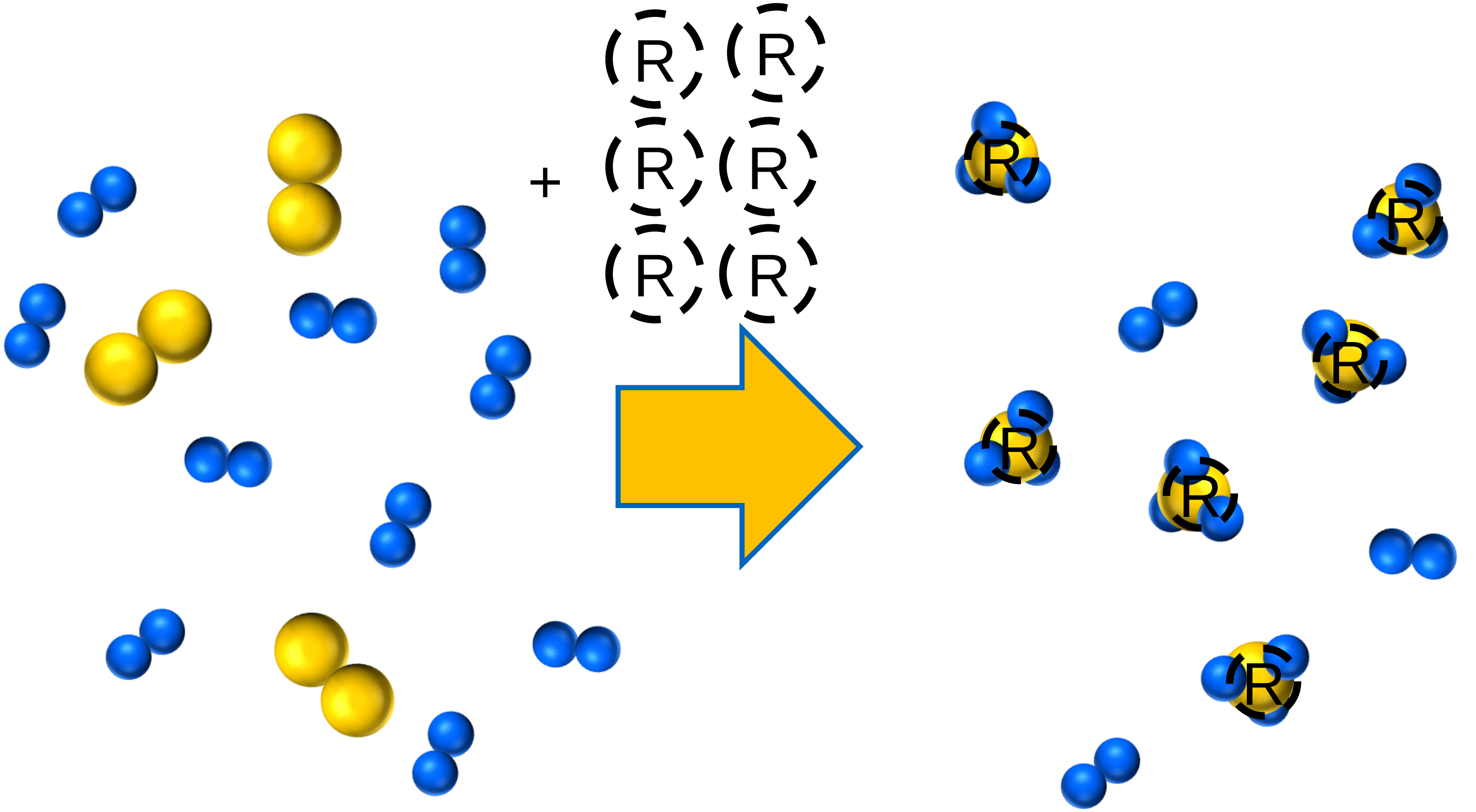
```
§
   3   1    3    2
 N                          H                         *R
 14.007                     1.008                     1e-05
6    1  2  3  4  5  6
2    1  2
gas
IDMX
N2(g)
 7  4    2.0   0.0   0.0
 0.0             191.6105
 350.0        29.29831        -1.567199E-03   3.418894E-06    -723.2298
 0.0
 700.0        27.75317        6.047626E-04    4.95983E-06     72832.12
 0.0
 1500.0       23.52867        0.01211645      -3.076219E-06   1.210385E+05
 0.0
 3400.0       35.36803        1.041014E-03    -1.111572E-07   -4.146351E+06
H2(g)
 7  2    0.0   2.0   0.0
 0.0             130.6789
 298.15       22.49577        0.01704385      1.112197E-05    36532.0
 0.0
 5000.0       25.85524        4.83665E-03     -3.7164E-07     1.58415E+05
NH3(g)
 7  2    1.0   3.0   1.0
 -45940.32       192.7778
 1000.0       24.90389        0.03632064      -4.608822E-06   48712.9
 0.0
 6000.0       65.06398        7.644131E-03    -8.509465E-07   -1.658366E+07
R+                       !
 1  1    0.0   0.0   1.0
 298.15       0.0             0.0             0.0             0.0
R-                       !
 1  1    0.0   0.0   -1.0
 298.15       0.0             0.0             0.0             0.0
```

Virtual feed phases

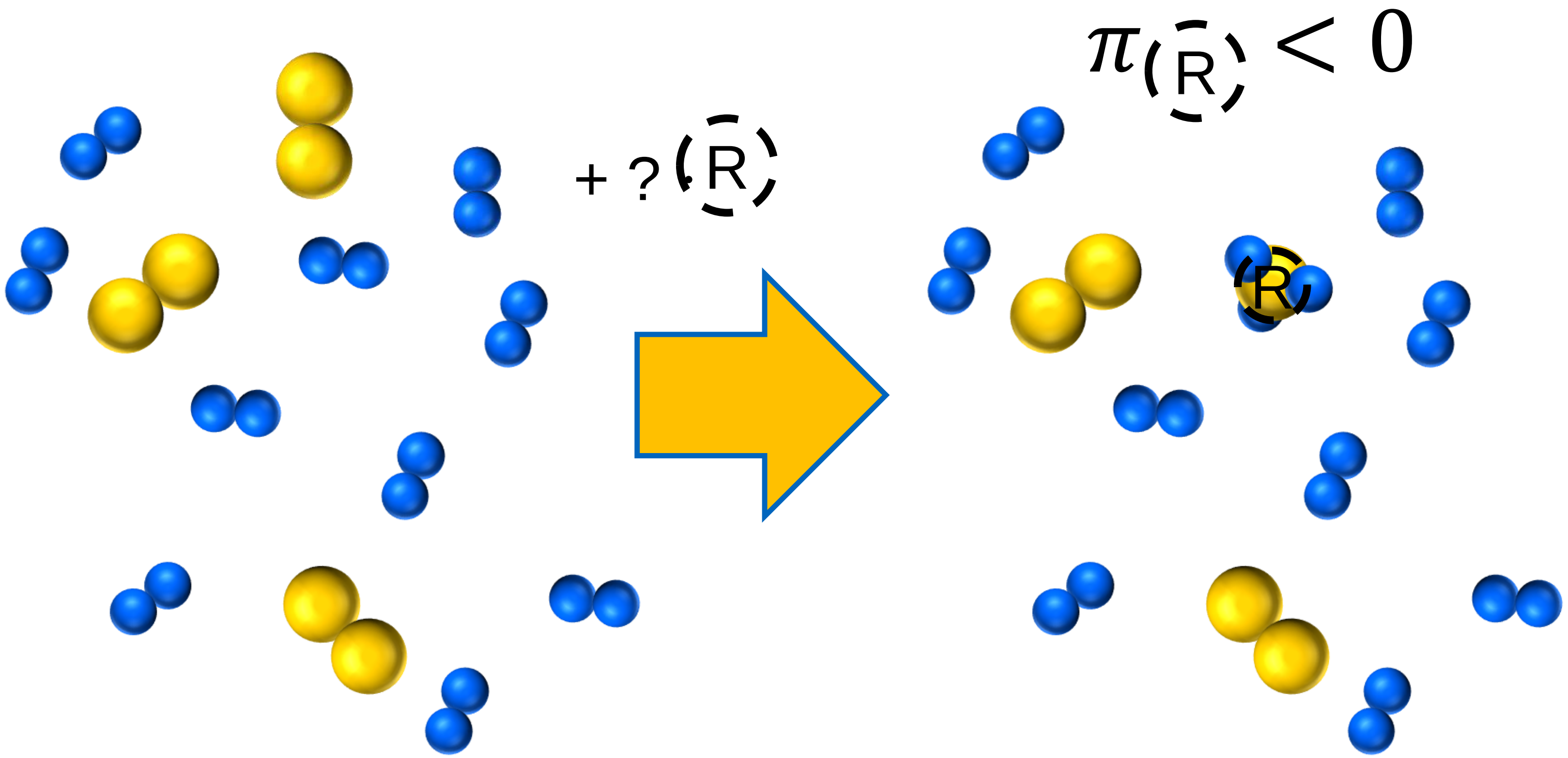
Controlling the extent of a reaction



Controlling the extent of a reaction

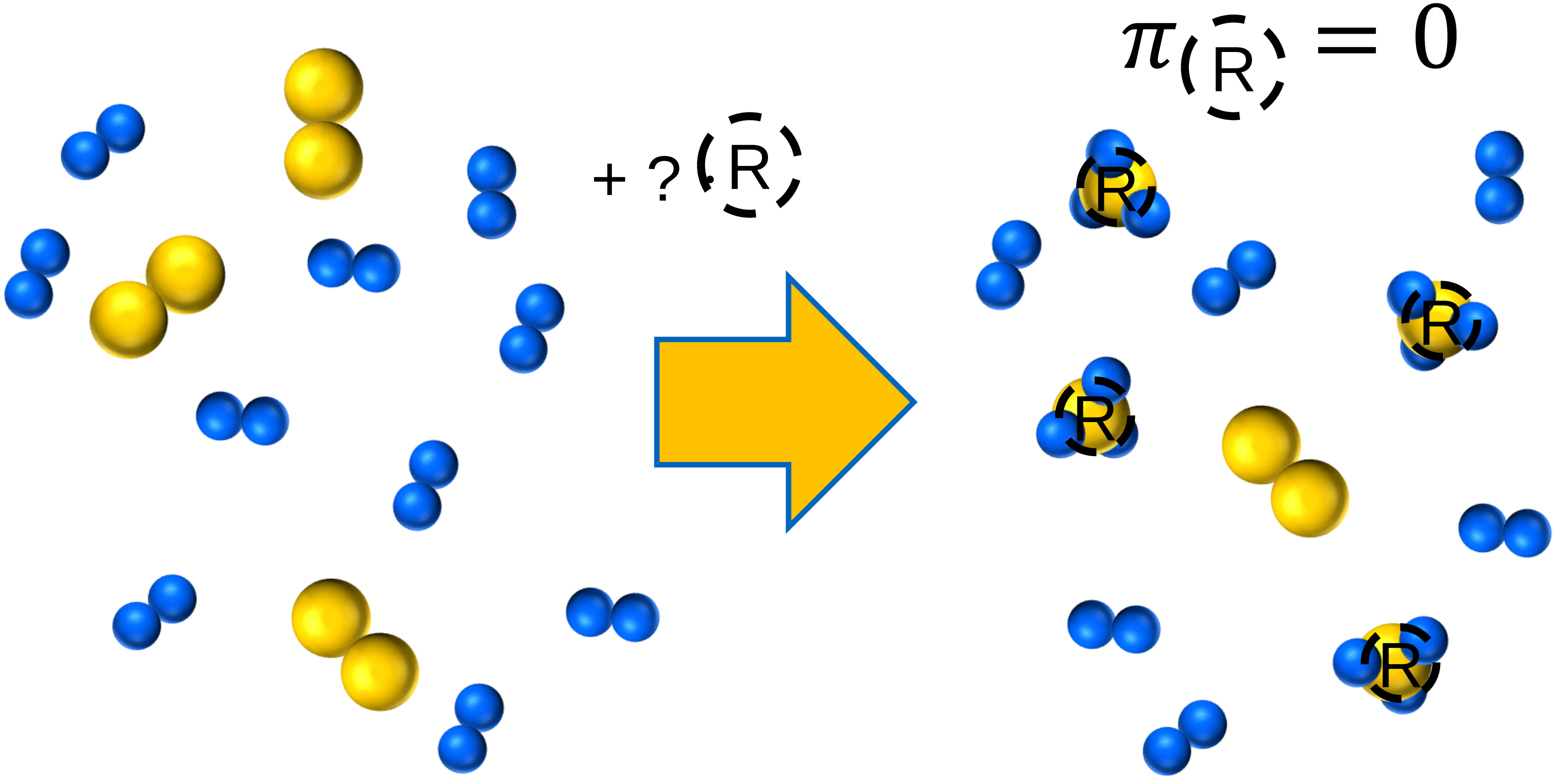


Controlling the extent of a reaction

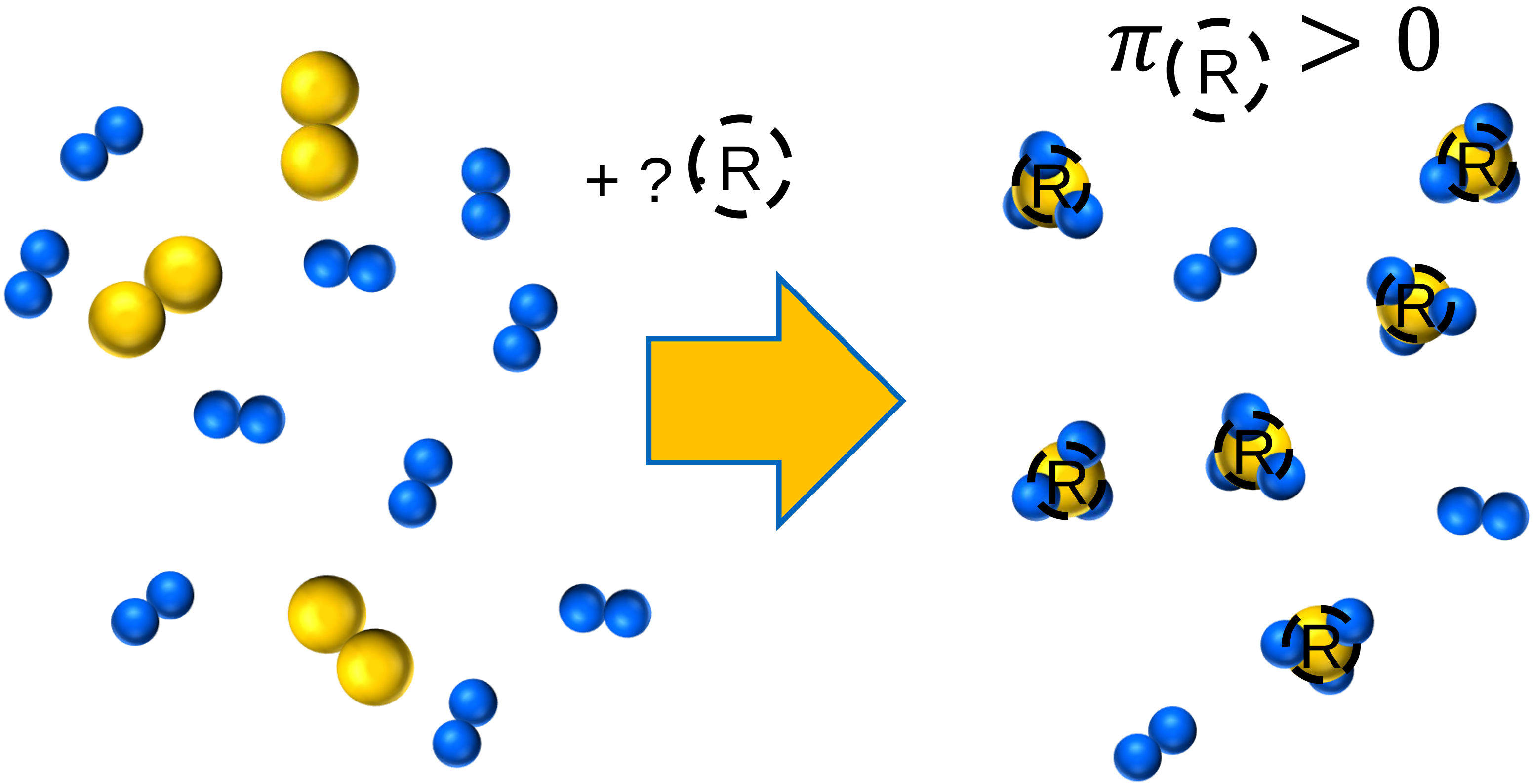


$$\pi_{R} < 0$$

Controlling the extent of a reaction

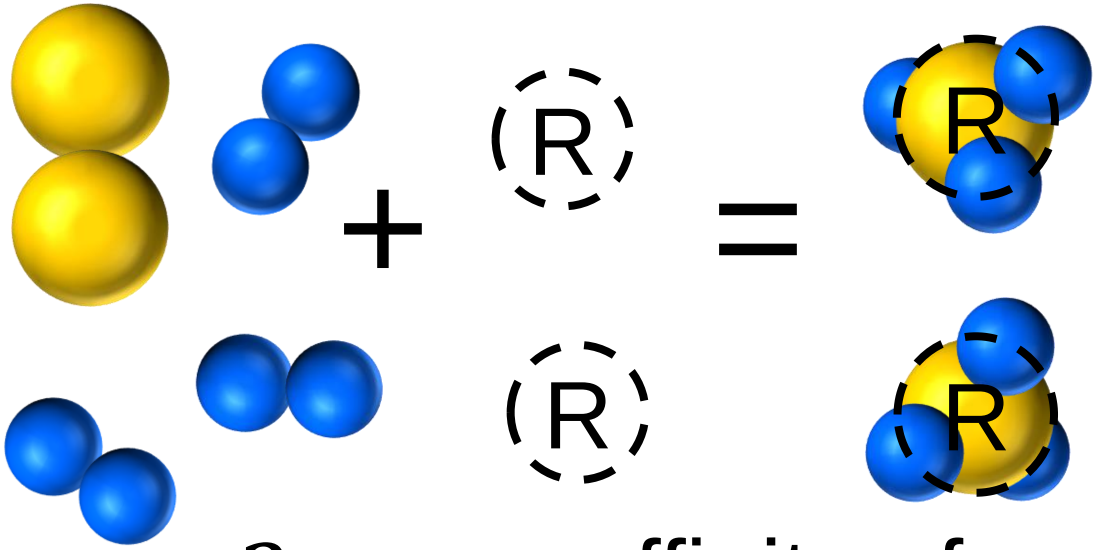


Controlling the extent of a reaction



Reaction affinity$(-\Delta G_r)$

$$N_2 + 3H_2 + 2\textcircled{R} \Leftrightarrow 2NH_3$$

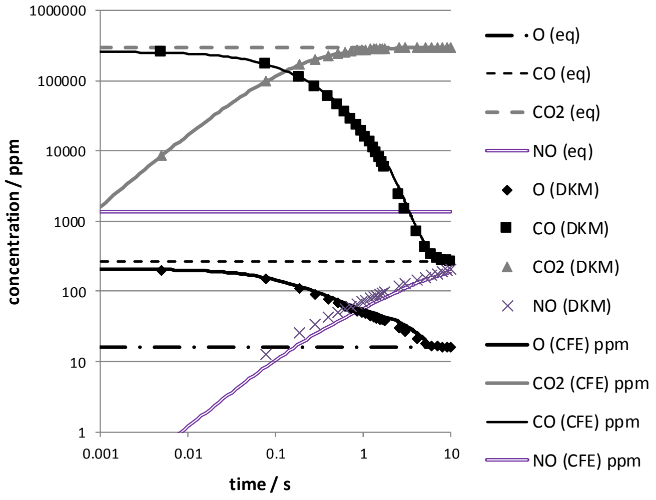


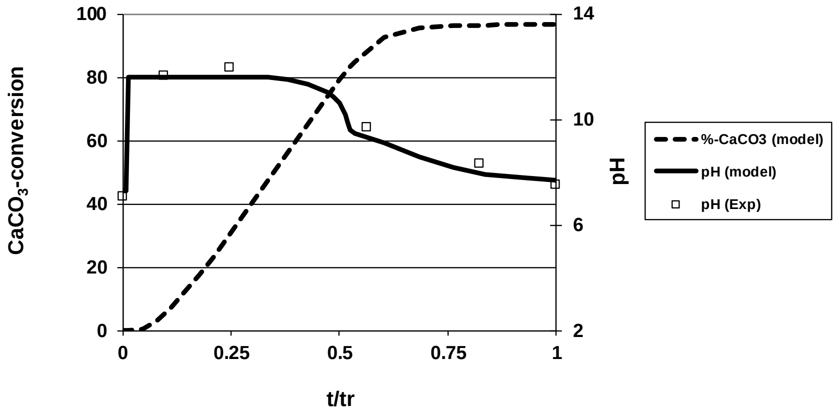
$$-2\pi_{\textcircled{R}}$$ = affinity of reaction

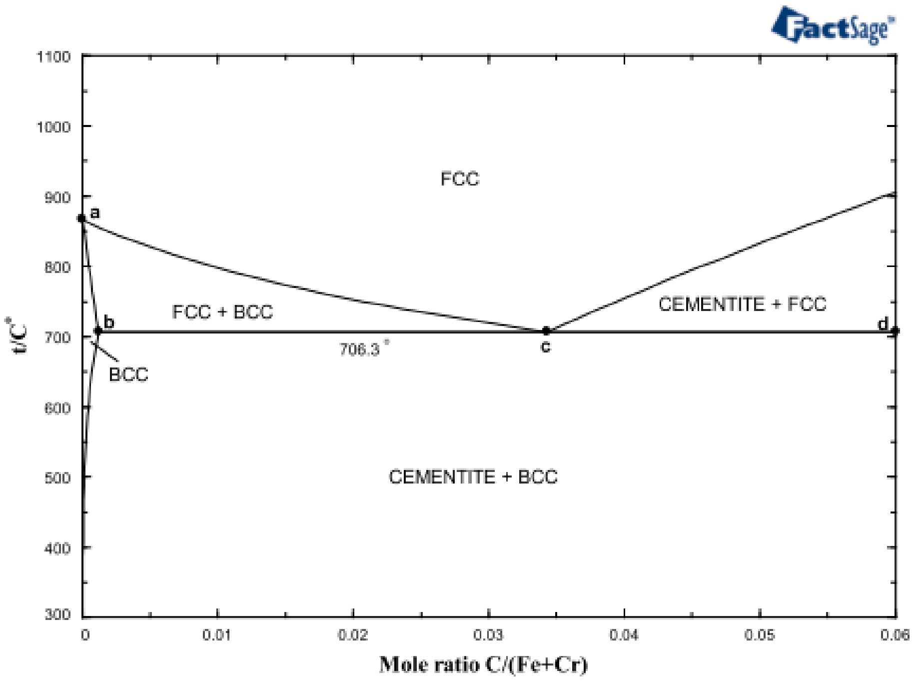
Reactive systems with more than one constrained reactions

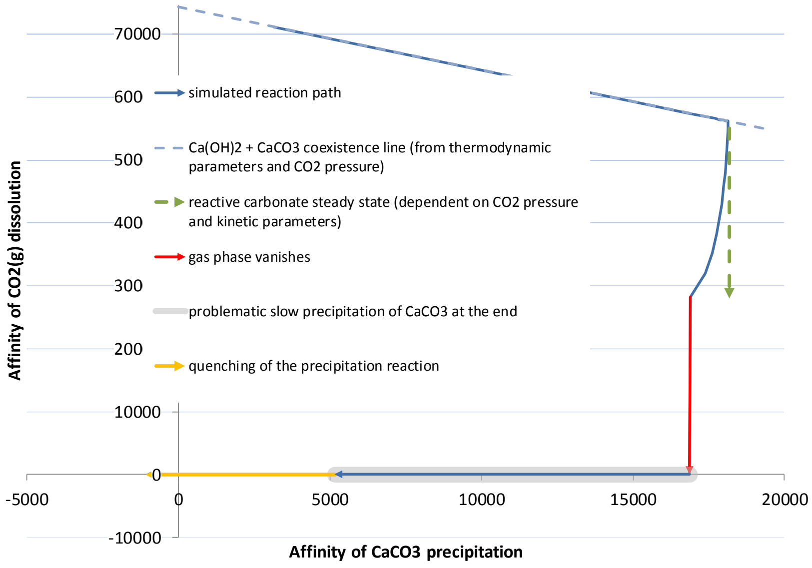
- More than one reaction extent can be controlled at the same time.
- In principle there is no other limitation here except the total amount of system components allowed in ChemApp
- In practical terms at VTT we have rarely used more than a few simultaneous reaction constraints at the same time. Typically if a problem requires handling of more elaborate kinetics, there are dedicated codes for that. When applying ChemApp one presumably has a system which is predominantly controlled by thermodynamics.

(Example results)









Work

Work = force $\cdot$ displacement

$$W = \int \partial E / \partial l \cdot dl$$

$$W = -\text{affinity} \cdot \text{change in reaction extent}$$

Work = force · displacement

$$W = \int \partial E/\partial l \cdot dl$$

$$W = -\int \mathbb{A} d\xi$$

Work = force · displacement

$$W = \int \partial E / \partial l \cdot dl$$

$$W = \int \pi_R db_r$$

$$(\pi_R = -\mathbb{A}; db_r = d\xi)$$

Is this valid also in more general? Is there a similar connection also in other kinds of systems between thermodynamic work and constraints set on the system?

Membrane equilibria

		H	O	e-	Na	Cl	A
V_1	H_2O	2	1	0	0	0	0
	H(+)	1	0	-1	0	0	0
	OH(-a)	1	1	1	0	0	0
	O_2(a)	0	2	0	0	0	0
	Na(+)	0	0	-1	1	0	0
	Cl(-a)	0	0	1	0	1	0
V_2	H_2O	2	1	0	0	0	0
	H(+)	1	0	-1	0	0	0
	OH(-a)	1	1	1	0	0	0
	O_2(a)	0	2	0	0	0	0
	Na(+)	0	0	-1	1	0	0
	Cl(-a)	0	0	1	0	1	0
	A(-)	0	0	1	0	0	1

Membrane equilibria

		H	O	e-	Na	Cl	A	z_2
V_1	H_2O	2	1	0	0	0	0	0
	H(+)	1	0	-1	0	0	0	0
	OH(-a)	1	1	1	0	0	0	0
	O_2(a)	0	2	0	0	0	0	0
	Na(+)	0	0	-1	1	0	0	0
	Cl(-a)	0	0	1	0	1	0	0
V_2	H_2O	2	1	0	0	0	0	0
	H(+)	1	0	-1	0	0	0	1
	OH(-a)	1	1	1	0	0	0	-1
	O_2(a)	0	2	0	0	0	0	0
	Na(+)	0	0	-1	1	0	0	1
	Cl(-a)	0	0	1	0	1	0	-1
	A(-)	0	0	1	0	0	1	-1

Work = force $\cdot$ displacement

$$W = \int \partial E / \partial l \cdot dl$$

$$W = \int \mathbb{A} d\xi$$

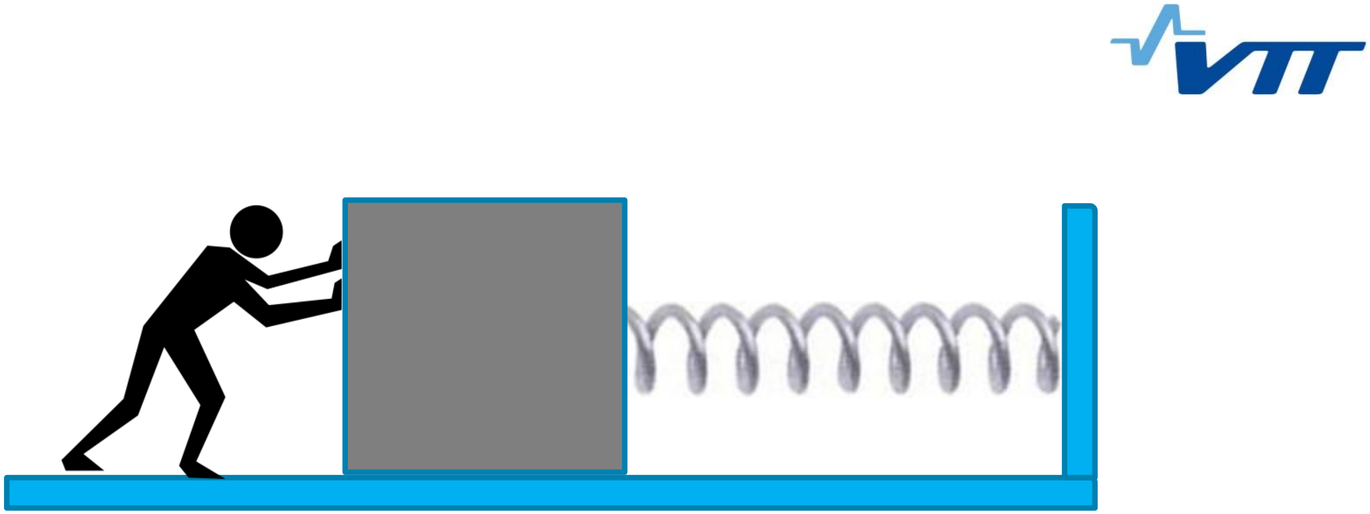
$$W = \text{electrical potential difference} \cdot \text{transferred charge}$$

Work = force $\cdot$ displacement

$$W = \int \partial E / \partial l \cdot dl$$

$$W = \int \mathbb{A} d\xi$$

$$W = -\int \Delta\psi dq$$



Work = force $\cdot$ displacement

$$W = \int \partial E / \partial l \cdot dl$$

$$W = \int \mathbb{A} d\xi$$

$$W = \int \pi_{z_2} d b_{z_2}$$

$$(\pi_{z_2} = -\psi F; d b_{z_2} = dq/F)$$

Osmotic pressure

		H	O	e-	Na	Cl	A	z_2	V_2
V_1	H_2O	2	1	0	0	0	0	0	0
	H(+)	1	0	-1	0	0	0	0	0
	OH(-a)	1	1	1	0	0	0	0	0
	O_2(a)	0	2	0	0	0	0	0	0
	Na(+)	0	0	-1	1	0	0	0	0
	Cl(-a)	0	0	1	0	1	0	0	0
V_2	H_2O	2	1	0	0	0	0	0	$V(H_2O)/V_0$
	H(+)	1	0	-1	0	0	0	1	0
	OH(-a)	1	1	1	0	0	0	-1	0
	O_2(a)	0	2	0	0	0	0	0	0
	Na(+)	0	0	-1	1	0	0	1	0
	Cl(-a)	0	0	1	0	1	0	-1	0
	A(-)	0	0	1	0	0	1	-1	0

Work = force $\cdot$ displacement

$$W = \int \partial E/\partial l \cdot dl$$

$$W = \int \mathbb{A} d\xi$$

$$W = \int \Delta\psi dq$$

$$W = \text{volume} \cdot \text{osmotic pressure}$$

Work = force · displacement

$$W = \int \partial E / \partial l \cdot dl$$

$$W = \int \mathbb{A} d\xi$$

$$W = \int \Delta \psi dq$$

$$W = V \Delta P$$

Work = force · displacement

$$W = \int \partial E/\partial l \cdot dl$$

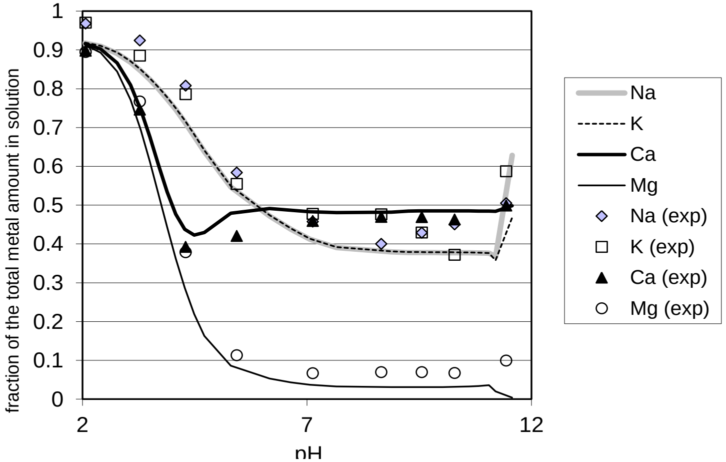
$$W = \int \mathbb{A} d\xi$$

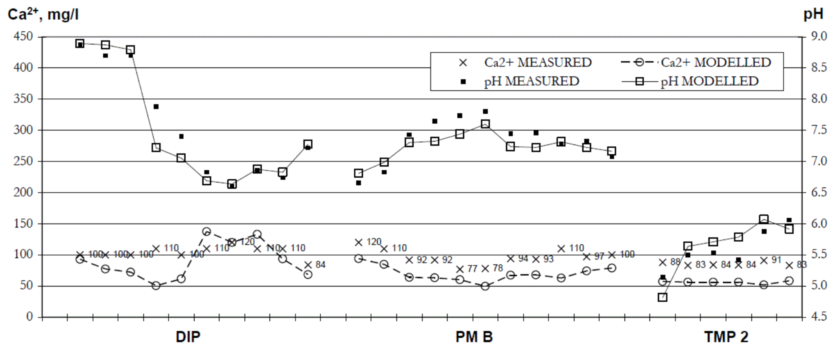
$$W = \int \Delta\psi dq$$

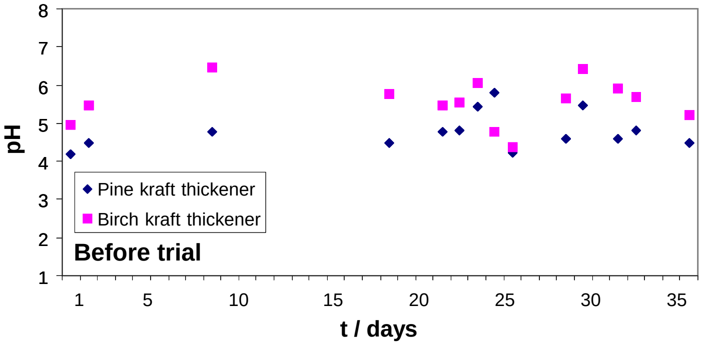
$$W = -\pi_{V_2} db_{V_2}$$

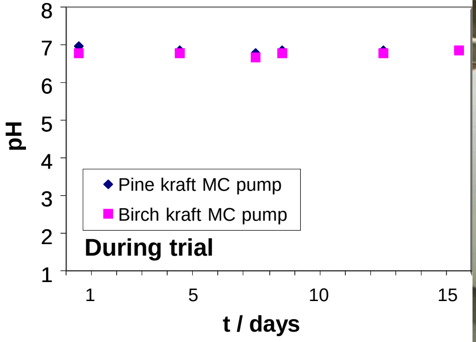
$$(\pi_{V_2} = -\Delta P \cdot V_0; db_{V_2} = V/V_0)$$

Membrane equilibria model applied in paper industry

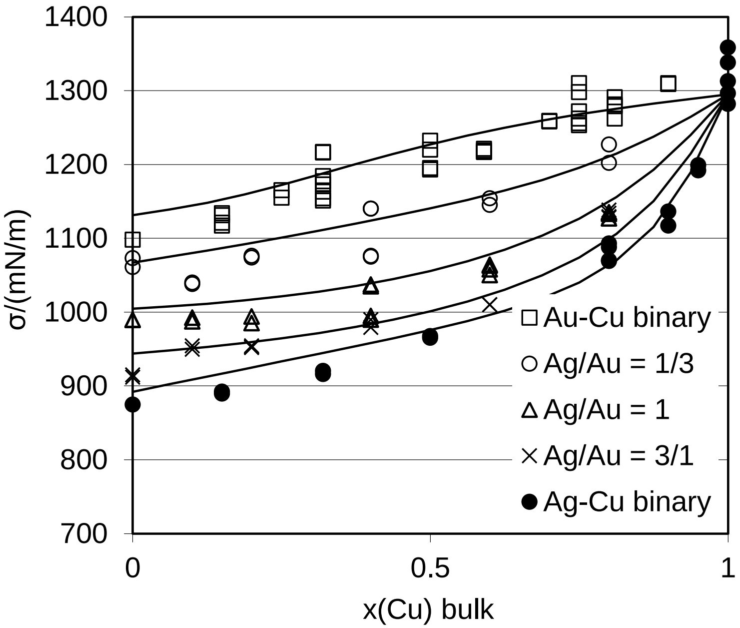


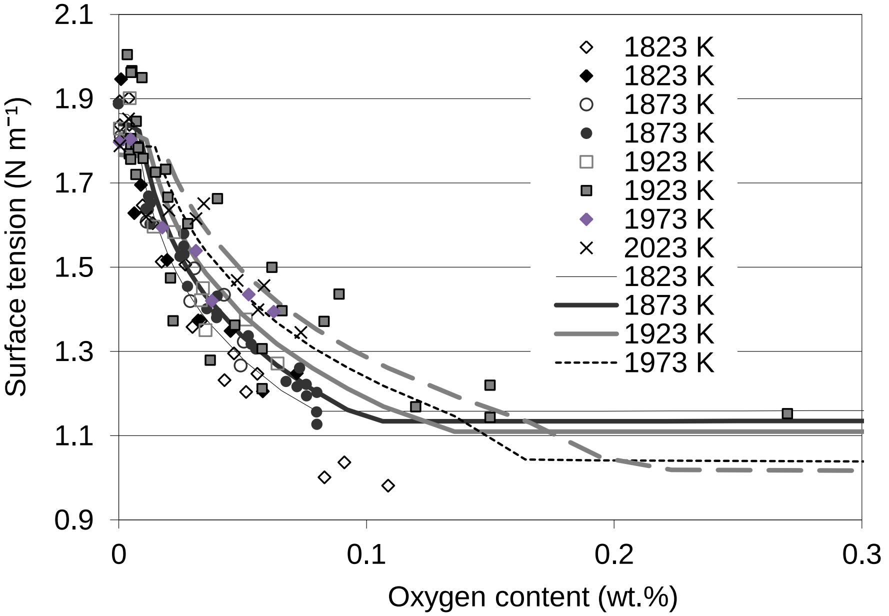






Surface energy





System stoichiometry

		Ag	Au	Cu	Area
bulk	Ag	1	0	0	0
	Au	0	1	0	0
	Cu(l)	0	1	1	0
surface	Ag	1	0	0	A_{Ag}/A_0
	Au	0	1	0	A_{Au}/A_0
	Cu	0	1	1	A_{Cu}/A_0

Work = force · displacement

$$W = \int \partial E/\partial l \cdot dl$$

$$W = \int \mathbb{A} d\xi$$

$$W = \int \Delta\psi dq$$

$$W = V\Delta P$$

$$W = \sigma A$$

Work = force · displacement

$$W = \int \partial E/\partial l \cdot dl$$

$$W = \int \mathbb{A} d\xi$$

$$W = \int \Delta\psi dq$$

$$W = V\Delta P$$

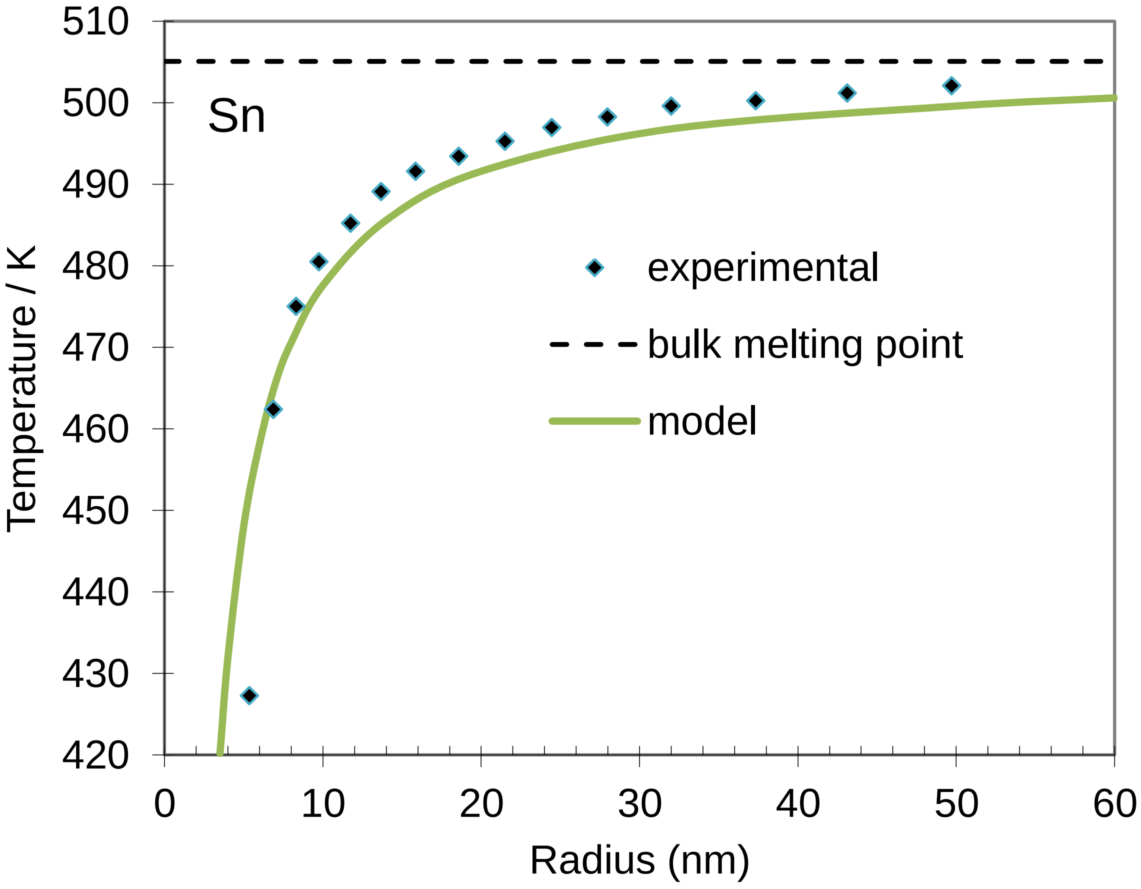
$$W = \pi_{Area} b_{Area}$$

$$(\pi_{Area} = \sigma A_0; b_{Area} = A/A_0)$$

Nanoparticle melting behaviour

$$dA = \frac{2dV}{r}$$

$$\sum_{\alpha} \sum_{i} dn_i^{\alpha} \left(A_i^{\alpha} - \frac{2V_i^{\alpha}}{r} \right) = 0$$



Work = force $\cdot$ displacement

$$W = \int \partial E/\partial l \cdot dl$$

$$W = \int \mathbb{A} d\xi$$

$$W = \int \Delta\psi dq$$

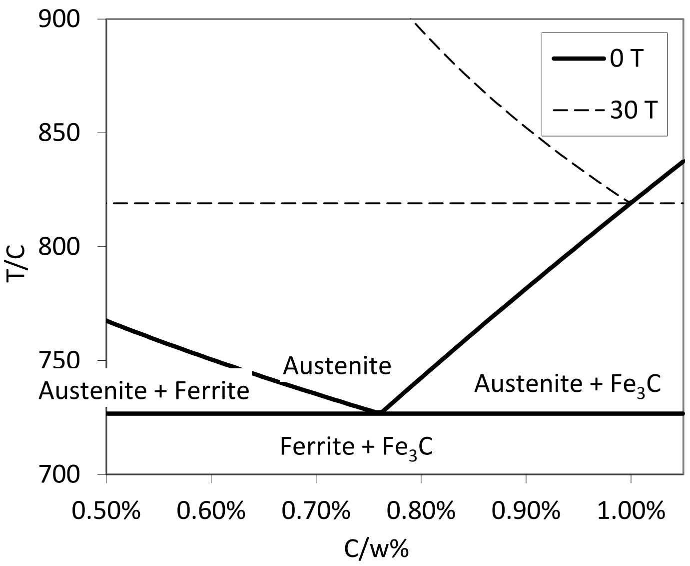
$$W = V\Delta P$$

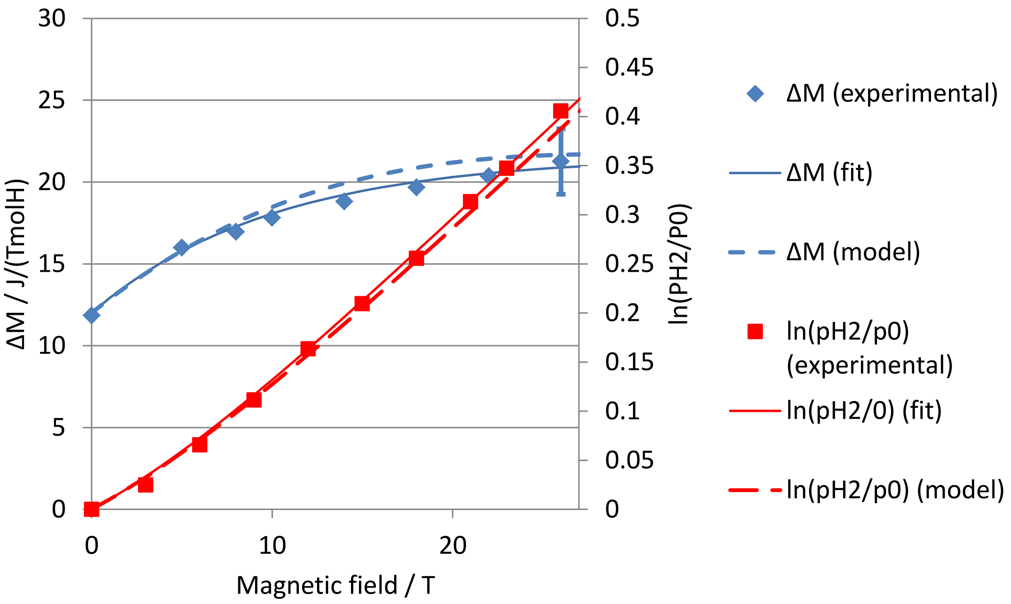
$$W = \sigma A$$

$$W = \int B dm$$

Effect of external magnetic field on phase stability

- Example cases Fe-C binary system and a LaCo-hydride. External field increases the stability of the strongly magnetizing phase.





Model with field dependent magnetic moment

- Assuming the magnetic moment can be factorized

$$m_i \equiv m'(B)m_i''$$

Stoichiometric coefficients for the new component are

$$a_{r,i} = \frac{m_i''}{m_j^0}$$

and the chemical potential set for the external magnetic fields

$$\pi_r = m^0 \int m' dB$$

Assuming that the magnetic moment has a constant (saturation) value, m' in the equations above can be set to unity

A summary

- In many cases one wants to set a new constraint to the system composition (such as fixed reaction extent, surface area, sub volume) of the linear form

$$\sum_i a_{ji} n_i - l_j$$

If the conserved quantity l_j does no have units of moles, the stoichiometric coefficients a_i are divided by normalisation factor a_j^0(with a constant but basically arbitrary value) so that we get unitless stoichiometric coefficients a_i' for the appended thermodynamic data file:

$$a_{ji}' = a_{ji}/a^0.$$

- For a problem with a fixed amount of the constrained quantity l_j of *extensive* nature the suitable input is then set in molar units as

$$l'_j = l_j / a_{\mathrm{j}}^0$$

- After the constrained equilibrium has been calculated the corresponding *intensive* property L_j of the system is obtained from the chemical potential of the constraining component as

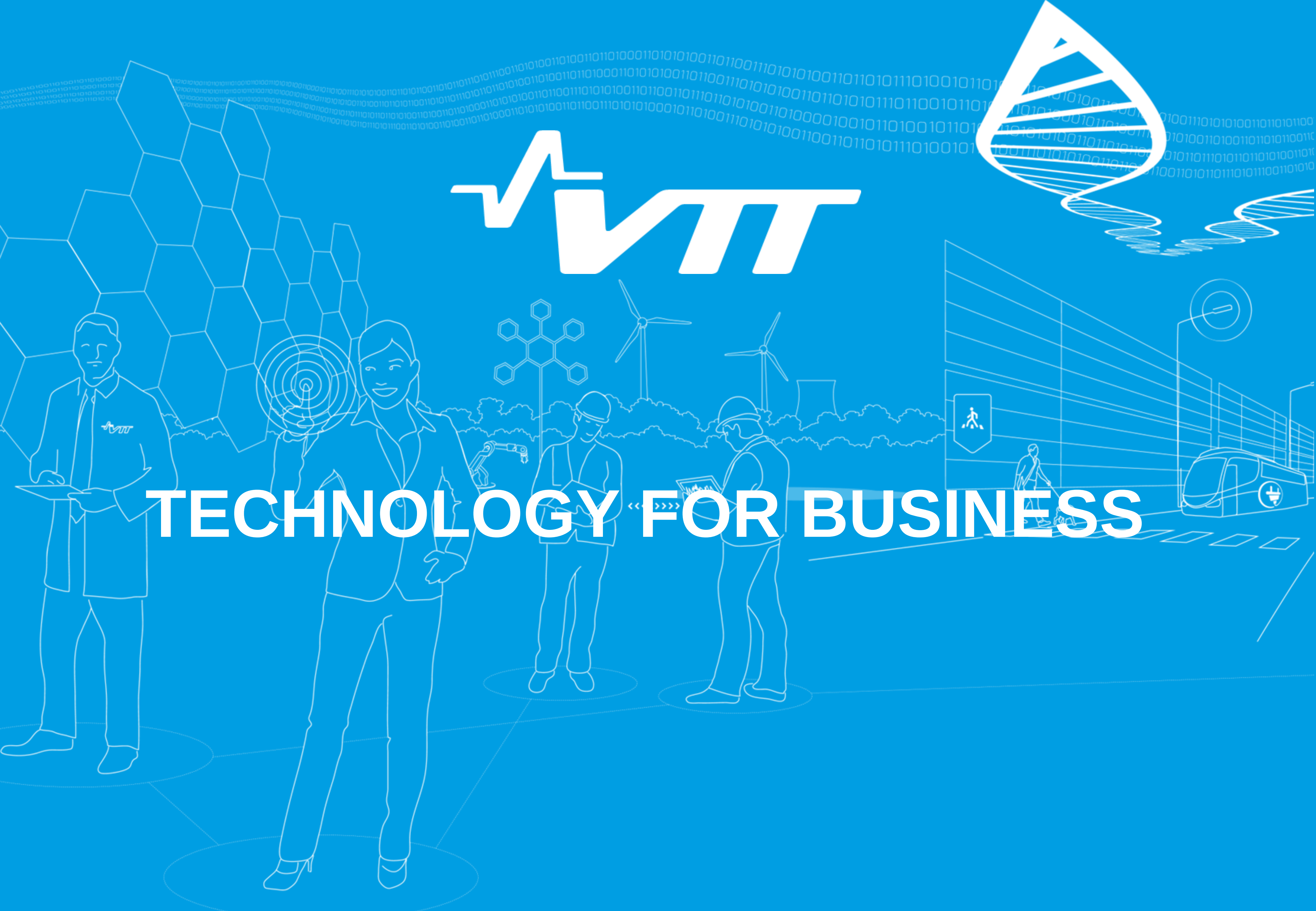
$$L_j = \pi_j a_j^0$$

so that

$$L_j l_j = \pi_j l'_j$$

Conclusions

- The area of applicability of ChemApp and ChemApp based programs has been extended by inclusion of additional constraining components.
- Most commonly these added constraints are either used to model systems that due to kinetic constraints do not reach full equilibrium (or do not do so immediately) or to add effect additional thermochemical work terms to the system
- Currently the extension require that the thermochemical data file is available in plain text format.
- Industrially applications done on areas of reaction rate controlled models, aqueous suspension models for paper & pulp industry and for calculation of surface tension of metallurgical mixtures
- Demonstration models done for nanoparticle phase stabilities and systems under external magnetic fields.
- Most of the material here discussed in the recent doctoral dissertation (Pajarre, R.“Modelling of chemical processes and materials by free energy minimisation. Additional constraints and work terms” Aalto University 2016) available online or by email risto.pajarre@vtt.fi



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