GEM-Selektor v.3-PSI Program Package – a Tool to Model Aqueous/Solid Solution Partitioning Equilibria

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- Sorption and co-precipitation are important mechanisms of redox-dependent chemical partitioning leading to retardation of radionuclides at waste repository conditions
- Adequate and efficient tools are needed for the equilibrium thermodynamic modelling of partitioning phenomena in aquatic geoenvironments
- That‘s why we develop the Gibbs Energy Minimization approach, implement it in GEM-Selektor program package, and use it!

Now available for downloading at http://les.web.psi.ch/Software/GEMS-PSI/

Thermodynamic Modelling

Thermodynamics is:

Easy to mention;

Difficult to understand;

Impossible to apply.

D.M.Shaw

- is a prediction of equilibrium speciation at certain physicochemical conditions and constraints in the system using methods of chemical thermodynamics

Reactions:	$r\rightarrow$	Chemical mass transfer
$\leftarrow r = r\rightarrow$	$A + B \leftrightarrow C + D$	$\leftarrow r \neq r\rightarrow$
at equilibrium	$\leftarrow r$	no equilibrium

To describe ***equilibria:***

- Mole quantities of chemical species in all phases are sufficient
- **Chemical reactions are not necessary to be considered**

The Equilibrium Problem Setup:

In reality




Ingredients **Recipe** **Cooking** **Done**

In terms of chemical thermodynamics:

at *T,P* of interest

Possible phases and components → **Initial state (bulk compo-sition mix, *b*)** → Equilibration, chemical mass transfer → **Final state *x* (meta)stable phases**

To solve for the equilibrium state

means to split the input bulk composition ***b*** into mole quantities ***x*** of species in all phases so that the total Gibbs energy of the system $G(x) = x^T \cdot \mu$ becomes minimal ($\mu = \mu^o + RT\,ln(C\gamma)$, $C = f(x)$ is concentration):

$$G(x) \Rightarrow \min$$
subject to $Ax = b$ (mass balance)

For multi-component systems, computer-aided numerical methods are required to solve for chemical equilibria. Available techniques:

- ***Law of Mass Action*** **(LMA)** method of speciation modelling (e.g. PHREEQC code)

$$|b - Ax| \Rightarrow \min \text{ at } LMA = f(K)$$

- ***Gibbs Energy Minimization*** **(GEM)** method of thermodynamic modelling (GEM-Selektor, ChemSage, GIBBS/Hch codes)

Complementarity of LMA and GEM techniques

LMA

- Gains in simplicity, balance precision, and speed
- Requires thermodynamic data (log*K*) for product species only
- Phases are not considered; a single solution phase assumed
- Sacrifices generality (difficult to set up and solve multi-phase, redox-dependent and SSAS equilibria).

GEM

- Gains in generality (easy to set up and directly solve multi-phase redox- or SSAS equilibria);
- Yields in balance precision and speed when using the automatic (simplex) initial approximation
- Requires thermodynamic data (G^o) for all species in all phases
- Phases are explicitly considered in finding species concentrations

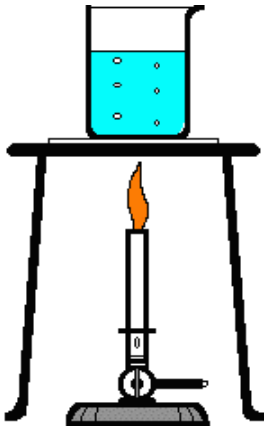
•Recently, speed and mass balance precision of GEM algorithm have been strongly improved.

•Now, precision in many cases is in GEM as good as in LMA codes.

•Attainable precision depends on the internal consistency of input thermodynamic data and also on the bulk composition (buffering capacity) of chemical systems.

GEM example: C-O-H-e aquatic system

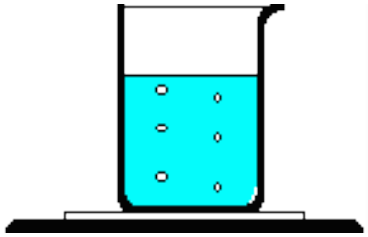
In the lab



***T*, *P* of interest:**

***T* = 25 °C**

***P* = 1 bar**



Ingredients: → **Initial State** (recipe) → **Equilibration** → **Final State** (speciation)

Water H_2O	300 g
CO_2	3 g
Carbon C	1 g

pH	?
pe/Eh	?
$\{CO_3^{-2}\}$	?
$f(CH_4)$	?

Water - Carbon System (C-H-O-e), input data + GEM results: I = 1.25e-4 pH=3.91 pe=-0.407

Input CSD	P= 1 bar, T= 25 °C	*b* vector, moles total	0.15143	33.305	16.7888	0	Primal solution (IPM)	
Phases	**Species**	$g^0/(RT)$, mol/mol	C	H	O	e	Vector *x*, mol	Vector v, mol/mol
Aqueous	CO2(aq)	-155.716	1	0	2	0	**1.021e-2**	-159.09
(8 + 1)	CO3-2	-212.984	1	0	3	-2	**1.48e-11**	-236.765
	HCO3-	-236.767	1	1	3	-1	**3.747e-5**	-245.77
	CH4(aq)	-13.859	1	4	0	0	**3.075e-9**	-32.26
	H2(aq)	+7.152	0	2	0	0	**2.32e-11**	-16.13
	O2(aq)	+6.635	0	0	2	0	**0**	-159.09
	OH-	-63.442	0	1	1	-1	**2.47e-11**	-86.674
	H+	0	0	1	0	1	**3.747e-5**	-9.003
	H2O(aq)	-95.677	0	2	1	0	**16.6525**	-95.677
Gas	CO2	-159.095	1	0	2	0	**5.792e-2**	-159.09
(4)	CH4	-20.4355	1	4	0	0	**4.27e-7**	-32.26
	H2	0	0	2	0	0	**5.71e-9**	-16.13
	O2	0	0	0	2	0	**0**	-159.09
Graphite	C	0	1	0	0	0	**8.326e-2**	0
Dual solution	*u* vector, mole/mole		**0**	**-8.065**	**-79.545**	**-0.938**	G(x) = **-1604.12354 mol**	

GEM-Selektor: A thermodynamic partitioning modelling tool

- Solves for phase speciation in heterogeneous systems involving any number of multi-component (non)ideal phases
- Considers surface species similarly to solid-solution end members, gases or aqueous species
- Gives a deep insight into mathematical structure of chemical equilibria expressed in terms of chemical elements, phases and species
- Two types of results (*primal* x and *dual* u) are obtained in one run of the convex programming algorithm
- The dual solution u enables for efficient retrieval of thermodynamic properties from experimental data

Total Gibbs energy

$$G(x) = \sum_{\Phi} \sum_{l_k} \mu_j x_j \quad \Rightarrow \min$$

$$\mu - A^T u \geq 0;$$

$$A\hat{x} = b; \quad \hat{x} \geq 0;$$

$$\hat{x}^T (\mu - A^T u) = 0.$$

DualT

$$\sum_{i \in N} a_{ji} u_i = \frac{g^o_{j,T}}{RT} + \ln C_j + \ln \gamma_j$$

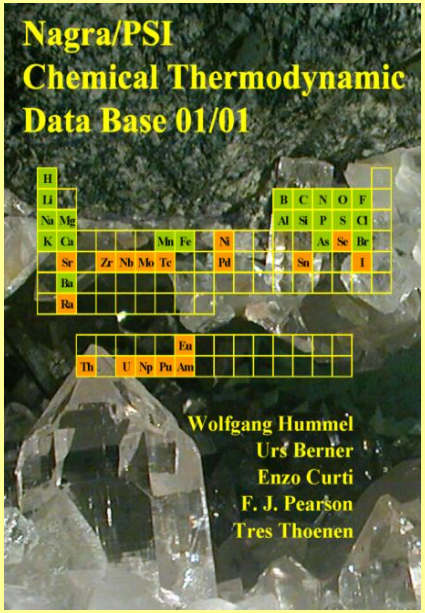
⟸ Karpov (Kuhn-Tucker) conditions

Chemical Thermodynamic Database: A **Consistency**

tedious never-ending work…

- **Standard molar properties** of all species: Nagra/PSI + Slop98.dat (T,Thoenen, D.Kulik, TM-44-03-04)
- **Temperature/Pressure corrections:** Thermochemical data, HKF EoS (aq)
- **DComp and ReacDC** record formats: GEMS default (kernel) database
- **Ionic strength corrections** (aq): Debye-Hueckel; SIT; Pitzer
- **Extensions:** more elements; surface species; organic complexes; SSAS …

Dual Thermodynamics?



Surface complexes of radio-nuclides;

Constants for host-mineral surfaces

GEM-Selektor v.3-PSI: What's next?

- **Yet more** user-friendly; Full tutorial suite; More input databases
- **GEM:** Coupling GEM IPM into mass transport codes
- **Intensive** and diverse applications at LES (waste management)
- **Worldwide** community of GEMS users; Going open-source GPL

Users feedback: a vital contribution for improving GEMS quality!