Thermochemical Simulations Based on Gibbs Energy Minimization

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A "simple" recipe

Take thermochemical property data for pure substances (e.g. Cu, Al_2O_3) (easy)

\+ Add thermochemical data for mixture phases (e.g. melts, slags, aqueous solutions, solid solutions) (difficult)

\+ Write a **Gibbs Energy Minimizing (GEM) Algorithm** to find the global minimum of all species considered (very difficult)

= Simulation method to model complex, real-life chemical processes (incredibly useful)

Calculation of complex (multi-component, multi-phase) equilibria

Many components, many phases (solution phases), constant T and p :

$$G = \min$$

with $$G = \sum_i n_i \mu_i = \sum_i n_i \left(\mu_i^o + RT \ln a_i \right)$$

or $$G = \sum_\varphi \left(\sum_i^{m_p} n_m^\varphi \right) G_m^\varphi$$

Modelling of Gibbs energy of (solution) phases

$$G_m^{\varphi} = G_m^{\varphi}\left(T, n_i^{\varphi}, p\right)$$

Pure Substance $G_m^{\varphi} = \mu^{o,\varphi} = G^{o,\varphi}(T,p)$ (stoichiometric)

Solution phase

$$\begin{aligned} G_m^{\varphi} &= G_m^{\varphi,ref} \\ &\quad + G_m^{\varphi,id} \quad \left(= -T\Delta S_m^{id}\right) \\ &\quad + G_m^{\varphi,ex} \end{aligned}$$

Choose appropriate reference state and ideal term, then check for deviations from ideality.

Observe mass balance constraint

$$\sum_i a_{ij} n_i = b_j$$

j = 1, ... , n of components b

a_{ij} → j

↓

i

Phase	Components	System Components						
		Fe	N	O	C	Ca	Si	Mg
Gas	Fe	1	0	0	0	0	0	0
	N_2	0	2	0	0	0	0	0
	O_2	0	0	2	0	0	0	0
	C	0	0	0	1	0	0	0
	CO	0	0	1	1	0	0	0
	CO_2	0	0	2	1	0	0	0
	Ca	0	0	0	1	0	0	0
	CaO	0	0	1	0	1	0	0
	Si	0	0	0	0	0	1	0
	SiO	0	0	1	0	0	1	0
	Mg	0	0	0	0	0	0	1
Slag	SiO_2	0	0	2	0	0	1	0
	Fe_2O_3	2	0	3	0	0	0	0
	CaO	0	0	1	0	1	0	0
	FeO	1	0	1	0	0	0	0
	MgO	0	0	1	0	0	0	1
Liq. Fe	Fe	1	0	0	0	0	0	0
	N	0	1	0	0	0	0	0
	O	0	0	1	0	0	0	0
	C	0	0	0	1	0	0	0
	Ca	0	0	0	0	1	0	0
	Si	0	0	0	0	0	1	0
	Mg	0	0	0	0	0	0	1

Example of a stoichiometric matrix for the gas-metal-slag system Fe-N-O-C-Ca-Si-Mg

Modelling and simulation tools

FactSage™

- **The Integrated Thermochemical Databank System**

→ ... to perform interactive and phase diagram calculations

ChemApp™

- **The Thermochemical Library** (Gibbs Energy Minimizer) for your Software

→ ... to add thermochemical equilibrium calculations to your or third-party software

SimuSage™

- **The Component Library for Rapid Process Modelling**

→ ... to create ChemApp-based complex process simulations with Borland Delphi®

Available thermochemical data

- **Compound databases**:
  > 4500 pure substances and stoichiometric compounds
- **Solution databases:**
  - Oxides
  - Salts
  - Metallic alloys
  - Light and noble metals
  - Steel, copper and lead alloys
  - Ultrapure silicon
  - Aqueous solutions
  - Nuclear materials
  - Pulp and paper