Thermodynamic Modelling of High Temperature System

Chemeca 2009

Winny Wulandari[1], Geoff Brooks[1],

M. Akbar Rhamdhani[1], and Brian J. Monaghan[2]

[1]Faculty of Engineering and Industrial Sciences, Swinburne University of Technology, Melbourne, VIC

[2]School of Mechanical, Materials, and Mechatronics, University of Wollongong, Wollongong, NSW

SWINBURNE UNIVERSITY OF TECHNOLOGY

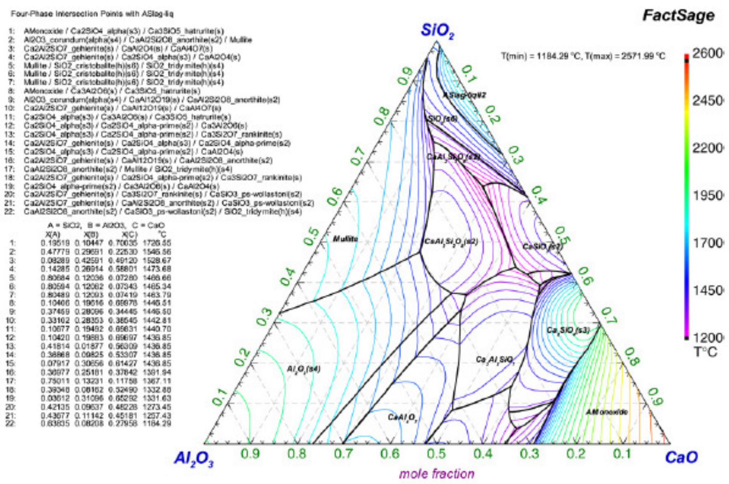
Content

- Introduction
- Gibbs Energy Minimisation
- Thermodynamic Modelling Development
- Thermochemical Packages
- Application

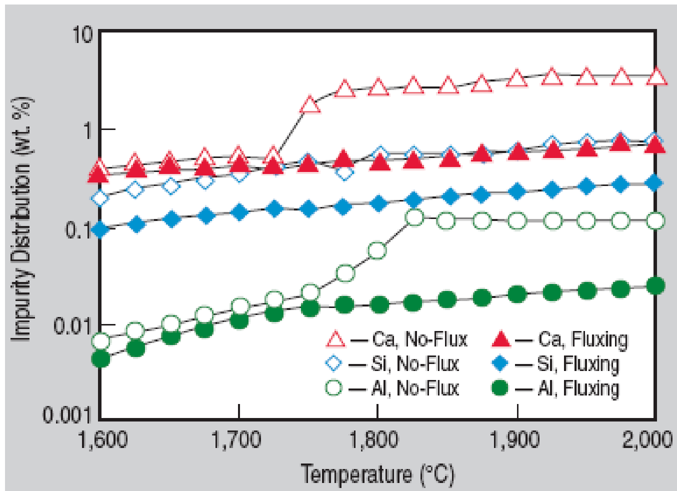
Introduction

- Thermodynamic modelling?
  - 2nd law thermodynamic :

    predict composition at equilibrium
- Purpose of thermodynamic modelling:
  - Predict chemical composition
  - Constructing phase diagram
  - Tool for process development



Bale *et al*, 2008



Brooks *et al*, 2006

Gibbs Energy Minimisation

- Based on Second Law Thermodynamics

$$G = \sum_{i=1}^{p} n_i G_i^{\phi} = \text{total free energy system} = \text{minimum};$$

$$\sum_{i=1}^{p} n_i a_{ji} = b_j; \text{mass balance constraint}$$

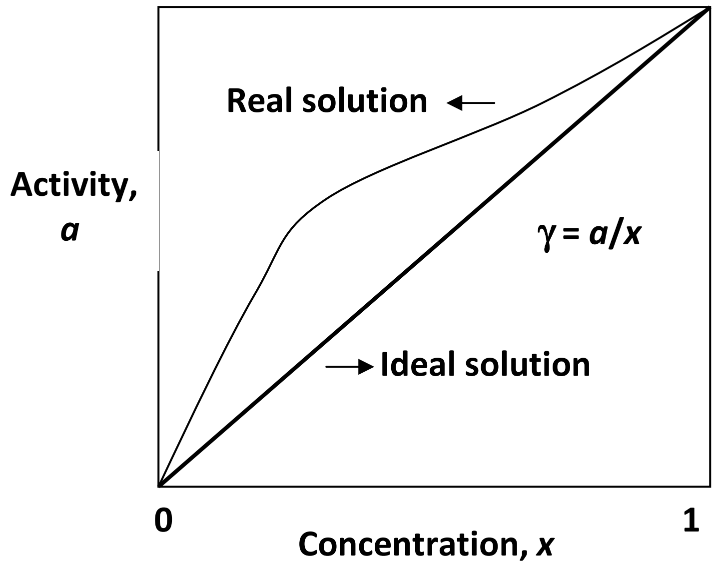
- Gibbs energy for real solution:

$$G^{\phi} = G^{o} + G^{ideal} + G^{ex}$$

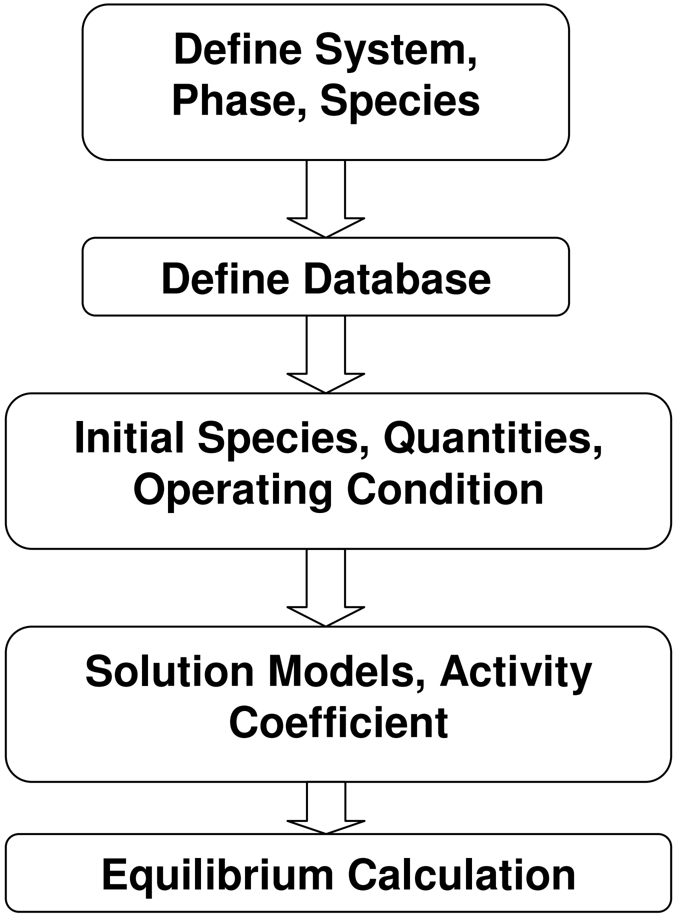
$$^{ideal}G^{\phi} = RT \sum x_i \ln x_i$$

$$^{ex}G^{\phi} = RT \sum x_i \ln \gamma_i$$

- γ_i, activity coefficient = f(x,T)



Development of Thermodynamic Modelling



Database

- Thermodynamic data: Enthalpy (H), Entropy (S), Heat Capacity (Cp), activity coefficient (γ)
  - Data taken from calorimetric measurement, Differential Thermal Analysis (DTA)
  - Activity coefficient data can be taken from Electromotive Force (EMF), Knudsen Cell, vapor pressure measurement
- Experimental data are assessed and modelled as function of temperature
  - $G = a + bT + cT\ln T + \Sigma dT^n$
  - $H = a - cT - \Sigma(n-1)dT^n$
- Example of database: SGTE (Scientific Group Thermodata Europe), FACT (Facility on Analysis of Chemical Thermodynamic)

Solution Models

In high temperature systems, it is common for species to dissolve and form multi-component phases: e.g. slags, matte, alloys

- ☐ Solution models have been developed to describe interactions in solutions

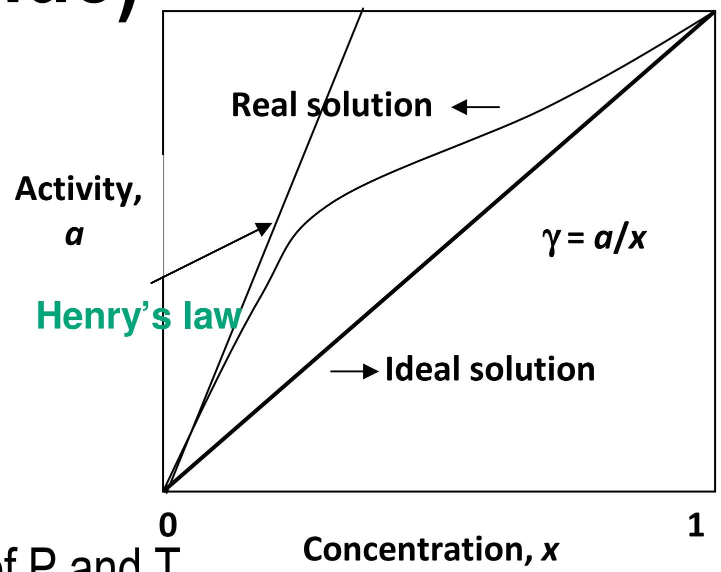
Some of example of solution model:

1. Ideal Solution Model
   - No interaction between molecules, $a = x$
   - Starting points to calculate thermodynamic modelling

Solution Models (continue)

2. Dilute Solution Model

- ☐ Henry's law: $a = \gamma^o_i x_i$
- ☐ γ^o_i: Henrian activity coefficient



3. Regular Solution Model

- ☐ Interaction parameter independent of P and T

$$^{ex}G^{\phi} = x_i x_j L$$

4. Random Mixing Solution Model

- ☐ For disorder substitutional solution
- ☐ Interaction between species is called excess term
- ☐ Redlich-Kister equation: $^{ex}G^{\phi} = x_i x_j \sum_{n=o}^{n=m} {}^{n}L^{\phi}_{i,j}(x_i - x_j)^n$

5. Compound Energy Formalism (Hillert, 2001)

- ☐ For crystalline that have 2 or more lattice structures.
- ☐ Can describe thermodynamic properties with interstitial and vacancy
- ☐ Basic formula:

$$G^{xs} = y_i y_j \sum_{k=0}^{n} L_{ij}^{S} \left(y_i - y_j \right)^k \qquad y_i^s = \frac{n_i^s}{N^s} \qquad x_i = \frac{\sum_s N^s y_i^s}{\sum_s N^s (1 - y_{Va}^s)}$$

6. Modified quasichemical model (Pelton *et al*, 2000)

- ☐ For short-range ordering solutions: molten slags, matte
- ☐ Formula: $G^{\text{liq}} = n_i^o G_i^{\text{liq}} + n_j^o G_j^{\text{liq}} - T\Delta S_C + \frac{n_{ij}}{2} G^{\text{ex,liq}}$
- ☐ ΔG_{ij} is noted as ($\omega - \eta T$)

Thermochemical Packages

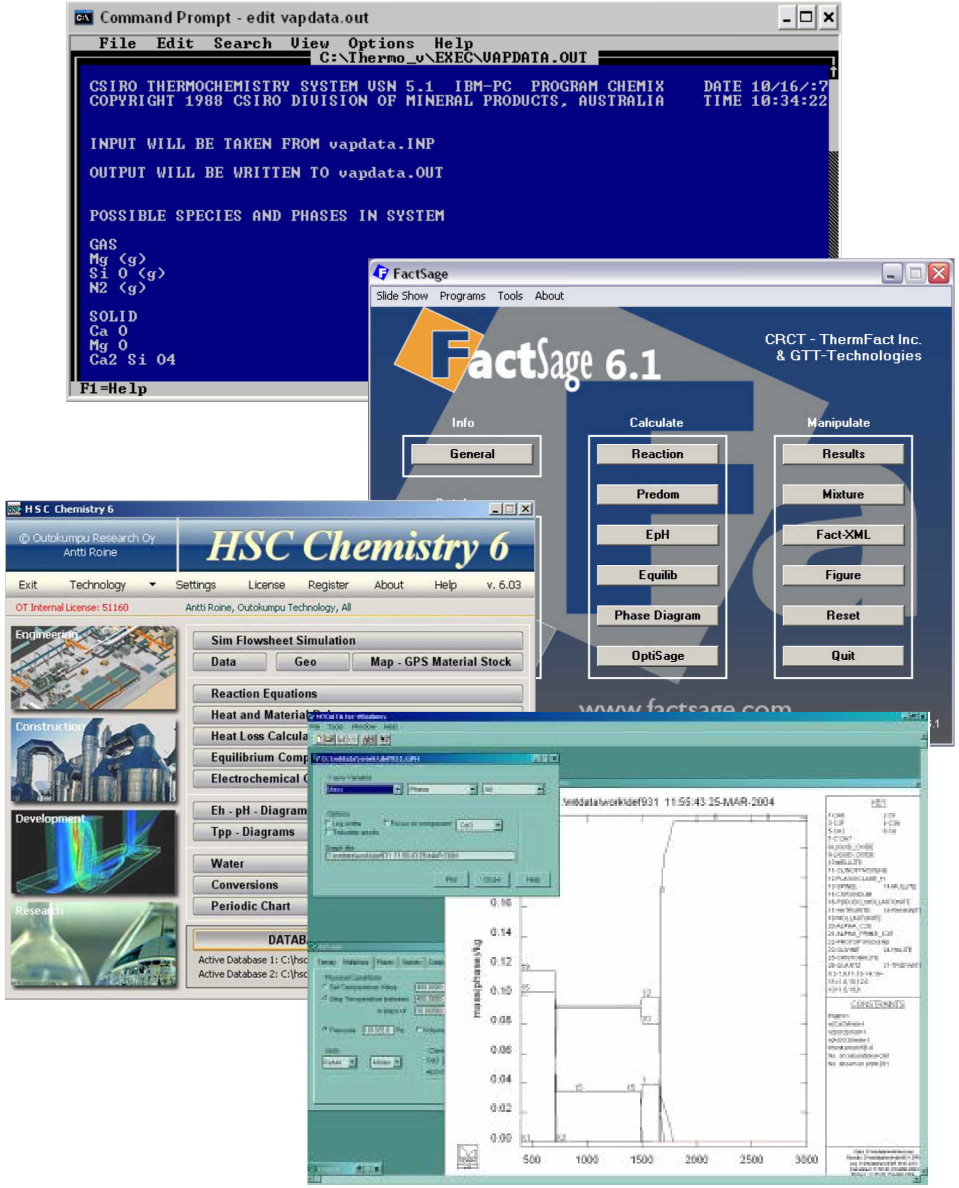
Chemix (CSIRO-SGTE

Thermodata System)

FactSage
(ThermFact Canada)

HSC Chemistry
(Outokumpu Finland)

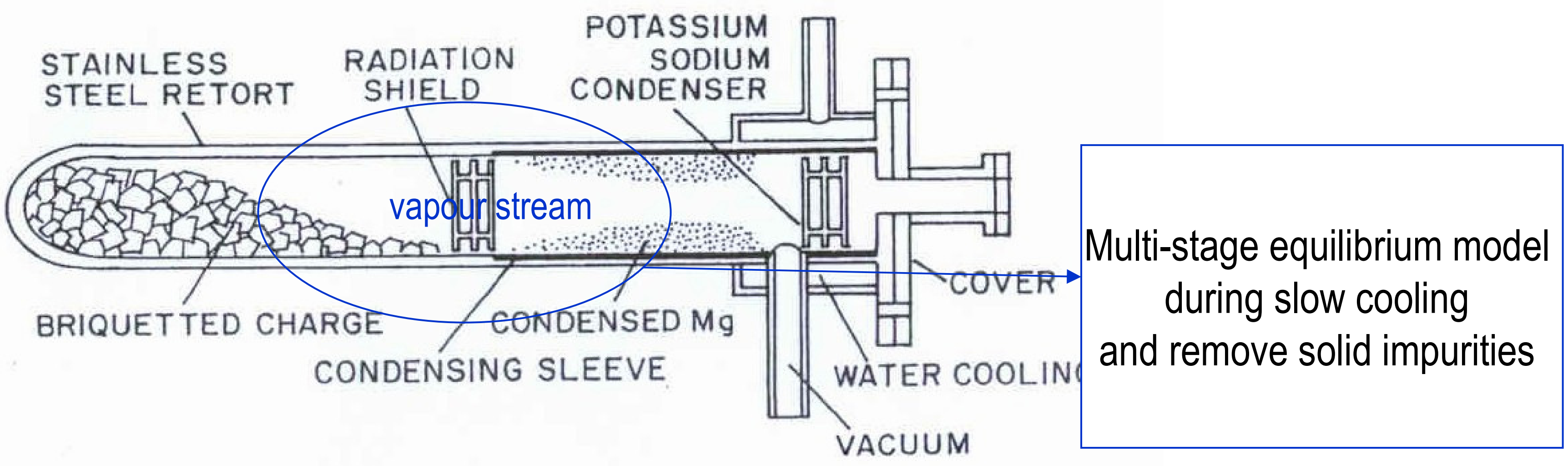
MTDATA
(NPL UK)



Comparison between Thermochemical Packages

Packages	Chemix	HSC	FactSage 6.1	MTDATA
Database	SGTE, JANAF, NPL	Barin, JANAF	SGTE 2009, FACT 2009	SGTE, NPL Database
Solution Models	Fixed, Polynomial, Debye-Huckel, Interpolation, Virial, Bethelot, Subregular, Redlich, Margules, Redlich-Kister, Lupis-Elliot, Virial Full, Pitzer, Redlich-Kister, Regular	-	Quasichemical, Sublattice, Pitzer, Polynomial (Muggianu), Polynomial (Kohler/Toop), CEF	associated solutions, CEF, Redlich-Kister polynomials, two-Sublattice ionic models, quasichemical model. Kapoo-Frohberg
Modules	Reaction, Equilibrium	Reaction, Equilibrium	Equilibrium, Phase Diagram, optimisation	Equilibrium, Phase Diagram, optimisation, solidification
Application interface	-	-	Yes	Yes (Matlab, Comsol)
Own solution data	Possible	-	Possible	Possible

Application: Thermodynamic Modelling of Pidgeon Process



Magnesium oxide is reduced by ferrosilicon to produce Mg vapour at 1160 C and 7 Pa

Reaction: 2 CaO.MgO + FeSi = 2 $Mg_{(g)}$ + Ca_2SiO_4 + Fe

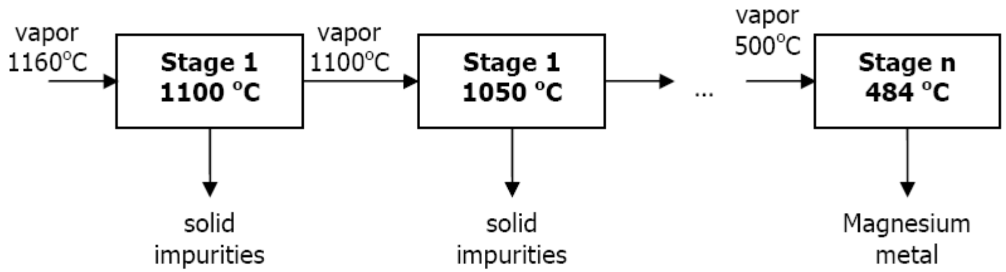
Magnesium vapor condensed in condenser

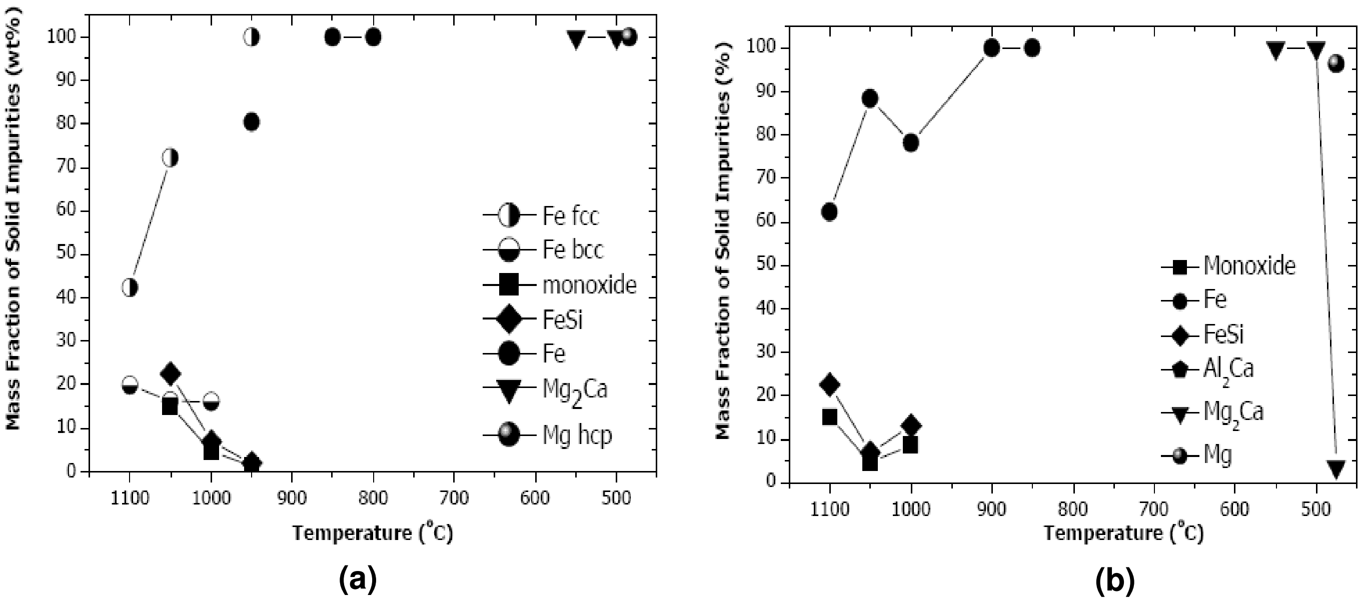
Phases and Solution Models in the Pidgeon Process

Phase	Solution Model	γ, activity Coefficient
Gas Phase: (Mg, Ca, SiO, Fe, Al)	Ideal Solution	$\gamma = 1$
Monoxide Phase (CaO, MgO, FeO, SiO_2)	Regular solution for MgO-FeO system	$\ln \gamma_i = L$
	Sub-regular for CaO-MgO system	${}^{ex}G^{\phi} = x_i x_j \sum_{n=0}^{n=m} {}^{n}L^{\phi}_{i,j}(x_i - x_j)^n$
Dicalcium silicate (Ca_2SiO_4, Mg_2SiO_4)	Random mixing Solution model for Ca_2SiO_4 and Mg_2SiO_4	
Metal Phase (Mg; Ca, Al, Fe, Si impurities)	First Assumption: Ideal Solution	${}^{ex}G^{\phi} = x_i x_j \sum_{n=0}^{n=m} {}^{n}L^{\phi}_{i,j}(x_i - x_j)^n$
	Second assumption: Random mixing solution model for fcc, bcc, and hcp solid solution.	

Solution model parameter metal phase were taken from existing literature (Lacaze & Sundman, 1991, Anglezio *et al*, 1994., Kevorkov *et al*, 2001, Islam & Medraj, 2005)

Thermodynamic Calculation of Mg Condensation





There are formation of solid impurities at temperature range between reaction zone and condenser zone.

-Ideal Solution: 98.33% Mg

-Random Mixing Solution: 99.98%

Mass Fraction of Solid Precipitated from Vapours Produced via the Pidgeon Process. At the Metal Phase (a) Using Random Mixing Solution Model, (b) Using Ideal Solution Model

Conclusion

- Thermodynamic modeling is valuable tool to predict phase equilibria in high temperature metals processing
- Thermo chemical packages makes modeling easier, but the fundamental knowledge such as how we determine the phase, species, and activity behaviour are the intellectual aspects
- An example in magnesium impurities illustrate both the predictive power of thermodynamic modelling but also the dilemmas associated with solution behaviour

Thank You