Condensed-phase Equilibrium for Ash-forming Fuels

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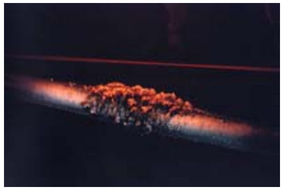
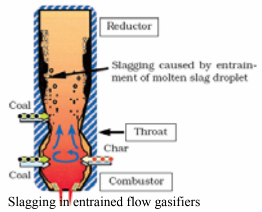
Background

- **Serious ash deposition/slagging dominates design and operation of thermal processors with ash-forming fuels.**
- **Phase equilibria and viscosity play a key role in deposit properties.**
- **Fusion temperature of ash/slags varies with composition.**
- **Thermodynamic models calculate slag melting points and compositions.**



Ash deposition on the surface of heat exchangers



Slagging in entrained flow gasifiers

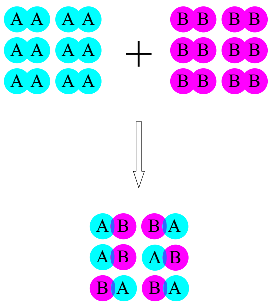
Objectives

- **Develop a thermodynamic model to correlate/predict high-temperature phase diagrams.**
- **Validate the model using available experimental data**

Modified Quasi-chemical Model

In a binary system composed of components *A* and *B*, the mixing Gibbs energy change can be accounted for by a quasi-chemical reaction:

(A-A) + (B-B) = 2 (A-B) Δg_{AB}



The Total Gibbs energy of the system is:

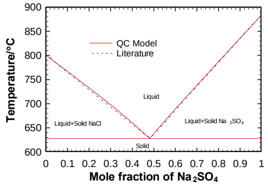
$$G = (x_A g_A^o + x_B g_B^o) - T\Delta S^{config} + (n_{AB}/2)\Delta g_{AB}$$

G: total Gibbs energy of the solution
T: temperature
x_i: mole fraction of the components
g_i^o: Gibbs energy of the pure component
ΔS^{config}: configurational entropy
n_{AB}: number of AB pairs in the solution
Δg_{AB}: nonconfigurational gibbs energy change

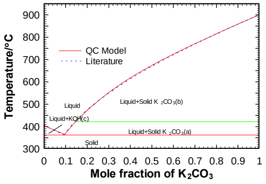
The Δg_{AB} term accounts for the Gibbs energy change due to the quasi-chemical reaction and is usually expressed as a polynomial function of x_i or mole fractions of A-A and/or B-B pairs. The coefficients of the polynomial function result from optimizing phase equilibrium and/or heat of mixing data.

Results

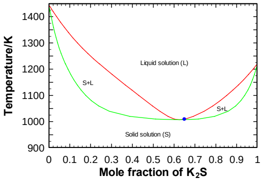
Binary Inorganic Salt Systems



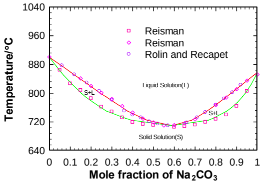
$NaCl-Na_2SO_4$



$KOH-K_2CO_3$

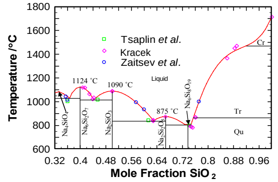


Na_2S-K_2S

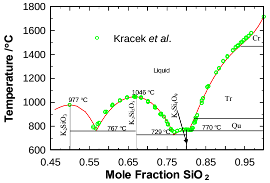


$Na_2CO_3-K_2CO_3$

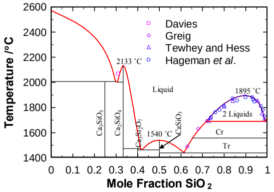
Silicate Systems



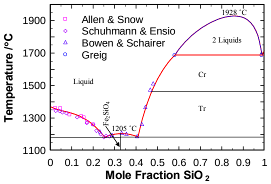
Na_2O-SiO_2



K_2O-SiO_2



$CaO-SiO_2$



$FeO-SiO_2$

Melting Points (MP) of Intermediate Compounds and Eutectic Points (EP) in Silicate Systems

Component	Calculated MP (˚C)	Literature MP (˚C)
K_2SiO_3	977	976−977
$K_2Si_2O_5$	1046	1045−1046
$K_2Si_4O_9$	770	769−771
Na_2SiO_3	1090	1090−1100
$Na_2Si_2O_5$	875	875
Na_4SiO_4	1085	1085
$Na_6Si_2O_7$	1124	1124
Ca_3SiO_4	-	1800−2149
Ca_2SiO_4	2133	2130−2145
$CaSiO_3$	1540	1540−1544

Type	Calculated EP		Literature EP	
	T (˚C)	$x(SiO_2)$	T (˚C)	$x(SiO_2)$
K_2SiO_3-$K_2Si_2O_5$	767	0.569	780−781	0.567
$K_2Si_2O_5$-$K_2Si_4O_9$	729	0.767	743	0.764−0.766
$K_2Si_4O_9$-SiO_2(Qu)	770	0.807	770	0.805
Na_4SiO_4-$Na_6Si_2O_7$	1029	0.367	1002	0.361
$Na_6Si_2O_7$-Na_2SiO_3	1015	0.442	1016	0.455
Na_2SiO_3-Na_4SiO_4	839	0.623	841−847	0.614−0.63
$Na_6Si_8O_{19}$-SiO_2(Qu)	804	0.747	794−799	0.742
Ca_3SiO_5-Ca_2SiO_4	2023	0.295	2057−2060	0.273−0.30
$Ca_3Si_2O_7$-$CaSiO_3$	1467	0.422	1450−1460	0.42−0.445
$CaSiO_3$-SiO_2(Tr)	1441	0.615	1441−1444	0.61−0.635

Many binary salt and silicate phase diagrams have been modeled and are available from the ash deposition group at Brigham Young University: $NaCl-Na_2CO_3$, $KCl-K_2CO_3$, $NaCl-Na_2SO_4$, $KCl-K_2SO_4$, K_2CO_3-KOH, $KCl-MgCl_2$, Na_2O-SiO_2, $CaO-SiO_2$, $Al_2O_3-SiO_2$, $FeO-SiO_2$, Na_2S-K_2S, etc.

Conclusions

- **A modified quasi-chemical model taken from the literature has been used to correlate phase diagrams of inorganic salts and silicates.**
- **The model has been validated using several binary systems.**
- **Thermodynamic properties of many pure compounds have been collected, approximated, or optimized.**
- **The results of the model in correlating low-order phases can be used in extrapolations to multi-component systems.**

Future Work

- **Expand the model validation to ternary and higher-order systems**
- **Collect and develop a database for the pure component properties and binary interaction parameters that can be used for multicomponent systems.**
- **Combine the phase equilibrium results with viscosity models to predict viscosities of slags in multi-component phases.**

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