TESTING AND APPLICATION OF COMMERCIAL THERMODYNAMICS SOFTWARE FOR SOLID-GAS EQUILIBRIA IN PLANETARY SCIENCE. J. W. Boyce[1], J.-M. Dudley[2], and D. Thompson[2], [1]Astromaterials Research and Exploration Science, NASA-Johnson Space Center, Mail Code XI3, 2101 NASA Pkwy Houston, TX 77058, USA, [2]Jacobs JETS II, NASA-Johnson Space Center, Mail Code XI3, 2101 NASA Pkwy Houston, TX 77058, USA.

Introduction: The ability to calculate chemical equilibria from thermochemical constants (e.g., H, S, Cp) or other experimental data is a tool widely employed by scientists. However, phase equilibria for planetary science problems is limited by easy access to libraries of thermochemical data, as well as the software to invert that data. Many academic software packages are focused on specific types of problems (e.g., aqueous solutions or melting and crystallization of magmas). This focus makes them excellent tools for specific uses, but poorer tools for other scenarios, especially those involving elements or chemical species that are less well-studied in that specific scientific field (e.g. NaCl vapor).

Amongst the more general thermodynamic software tools, there are closed academic software packages, open-source options, as well as commercial software. We have explored the extent to which commercial chemistry/chemical engineering software may be able to satisfy the need for thermochemical modeling packages that can accommodate the diverse species and conditions of planetary science problems. Here we compare the output of software package HSC Chemistry™ (Metso Outotec) to published vapor-solid phase diagrams for a variety of major and minor elements [1].

HSC Chemistry™ has been used in several recent geochemical studies of terrestrial volcanic systems [2-4]. However, it has not to our knowledge been benchmarked against peer-reviewed model results for the conditions and compositions relevant to planetary science. We present one such comparison here, the low-pressure environment of the solar nebula, using literature data. In short, we find excellent agreement between HSC Chemistry™ and the well-regarded academic software package CONDOR [1]. These preliminary results suggest that at least some commercial software packages are capable of robust thermochemical calculations for planetary science.

Experimental Design: We selected the calculations made on Solar System compositions using CONDOR [1] for this test for the following reasons: 1) The bulk chemistry is well-described for all elements; 2) The species used in the modeling are thoroughly documented; 3) Results are provided for a selection of major and minor elements; 4) The models lack silicate liquids (melts) which constitute an additional complication that we deemed unsuitable for this preliminary test.

The HSC Chemistry™ Gibbs Equilibrium Module (GEM) was used to calculate the abundances of solid and vapor species for Solar System abundances [5] as a function of temperature at 10^{-4} bars, to facilitate direct comparison with published results [1]. Solid-solution with ideal mixing is allowed where appropriate (e.g., feldspars, clino- and orthopyroxenes, amphiboles).

Results: Species abundances for individual elements (i.e., all the species that contain at least that element) are plotted against temperature for the following elements: Mg, Si, Fe, Ti, Ca, and S. NB: Species are reported here with the notation used in the HSC Chemistry™ database (e.g., *2CaO*Al2O3*SiO2 instead of $Ca_2Al_2SiO_7$ for gehlenite).
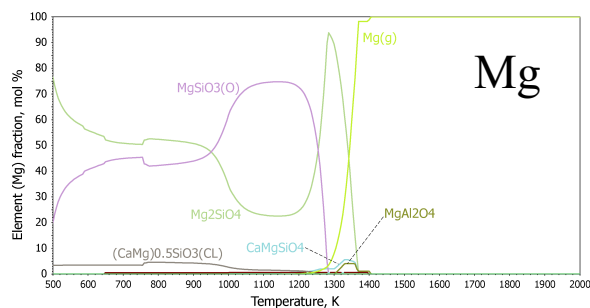

Magnesium. GEM and CONDOR yield similar model output for Mg, with Mg distribution dominated by an enstatite component in orthopyroxene and a forsterite component in olivine. Differences include a small $CaMgSiO_4$ component in olivine and lower stability of calcic clinopyroxene in GEM, as well as a small (<5%) stability field for $MgAl_2O_4$ in GEM that is not observed in CONDOR output, and a similar $MgCr_2O_4$ field observed in CONDOR that is not present in GEM. The origin of the spinel discrepancy is unknown.
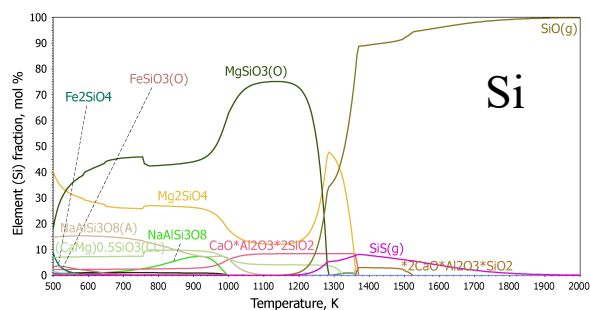

Silicon. For Si-bearing species at the ~5% modal abundance level or higher, GEM predictions are very similar to CONDOR. This includes a peak in the

abundance of forsterite at ~1300 K, as well as the appearance of vapor species SiO and SiS at T ≥ 1200 K. GEM partitions albite into two phases (alkali feldspar and plagioclase), but the total abundance is comparable to that of CONDOR.
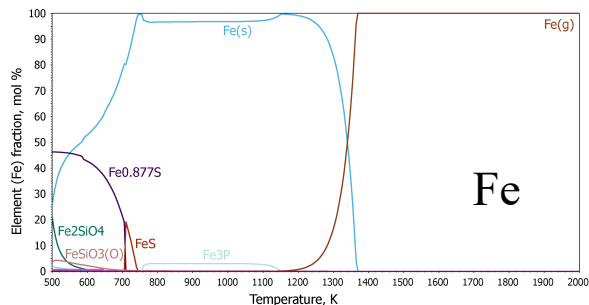

Iron. GEM and CONDOR differ in which iron sulfide phase is stable at low temperatures, but other phases/species are very similar in the output of the two models. Fe(s) dominates from 700-1300 K, with ~100% of Fe present as Fe(g) above 1300 K.
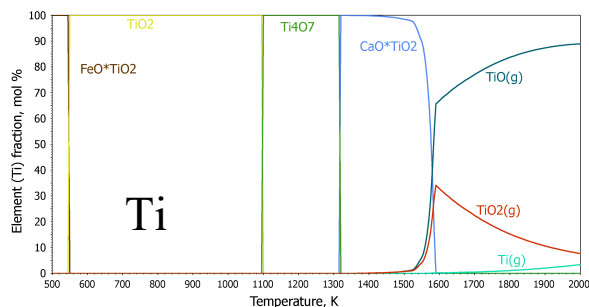
Titanium. GEM and CONDOR yield similar model output for all 7 species present. Ti is present as a combination of Ti(g), TiO(g), and TiO_2(g) above ~1550 K, with the fraction of TiO_2 decreasing as T rises.
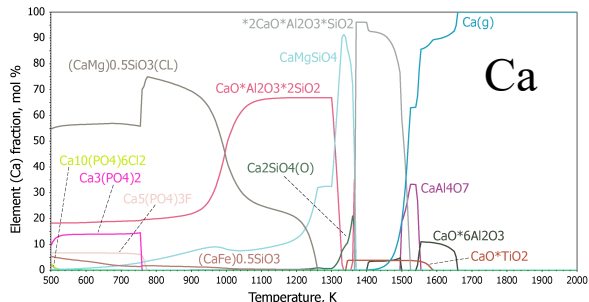
Calcium. GEM and CONDOR yield similar model output for most major Ca-bearing species, with the exception of Ca- and CaMg-olivine components stable in GEM. These species disappear from the assemblage if ideal mixing is turned off for olivine and all olivine components are required to saturate as separate phases. Clinopyroxene (T < 1000 K), plagioclase (1000-1350 K), and ghelenite (1350-1500 K) constitute more than 50% of the solid assemblage. Ca(g) vapor first appears at ~1450 K and comprises 100% of the Ca above ~1650 K.
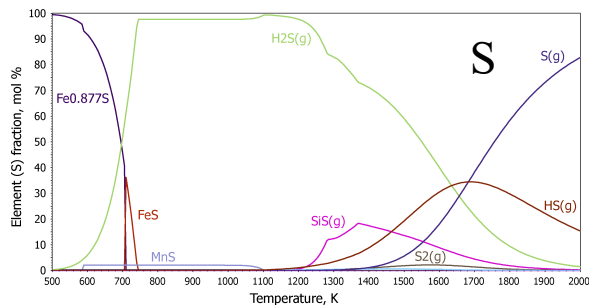
Sulfur. GEM and CONDOR yield similar model output for all phases excepting FeS (which in GEM is observed as a combination of $Fe_{0.877}S$ and FeS, as mentioned above). Above ~1200 K the fraction of S present as H_2S decreases, with first SiS(g), then HS(g), then S(g) as the prevent species, with only a small amount of S_2(g).

Discussion: Output from GEM is consistent with CONDOR, strong evidence that HSC Chemistry™ can be applied to planetary science problems. HSC Chemistry™ also permits the user to implement their own composition- and temperature-dependent activity models, as well as supplementation or modification of the thermodynamic database provided. These features should further increase the utility of HSC Chemistry™ for geochemical and planetary science applications.

References: [1] Fegley, B. and L. Schaefer, *Cosmochemistry*, in *Principles and Perspectives in Cosmochemistry*. 2010, Springer. p. 347-377. [2] Roberts, T., R. Martin, and L. Jourdain, *Reactive bromine chemistry in Mount Etna's volcanic plume: the influence of total Br, high-temperature processing, aerosol loading and plume–air mixing.* Atmospheric Chemistry and Physics, 2014. **14**(20): p. 11201-11219. [3] Rüdiger, J., et al., *Halogen activation in the plume of Masaya volcano: field observations and box model investigations.* Atmospheric Chemistry and Physics, 2021. **21**(5): p. 3371-3393. [4] Mason, E., et al., *Volatile metal emissions from volcanic degassing and lava–seawater interactions at Kīlauea Volcano, Hawai'i.* Communications Earth & Environment, 2021. **2**(1): p. 1-16. [5] Lodders, K. and B. Fegley, *The Planetary Scientist's Companion.* 1998: Oxford University Press, Incorporated.