

KNOWLEDGE GAPS IN APPLYING CONDENSATION CALCULATIONS TO CHONDRITES. L. Grossman (yosi@uchicago.edu)^{1,2} and A. V. Fedkin¹, ¹Dept. of the Geophysical Sciences and ²Enrico Fermi Institute, The University of Chicago, 5734 South Ellis Ave., Chicago, IL 60637.

Refractory Inclusions: (1) Equilibrium thermodynamic calculations applied to a system of solar composition at total pressures relevant to the inner solar nebula predict the first condensates from a cooling nebular gas to be corundum, hibonite ($\text{CaAl}_{12}\text{O}_{19}$), perovskite, grossite (CaAl_4O_7), dmitryivanovite (CaAl_2O_4), melilite, spinel, diopside and anorthite. Which of the above calcium aluminates become stable and in which sequence with falling T depend critically on thermodynamic data. The very high temperatures of stability ($>2073\text{K}$) of these phases lead to uncertainty in their liquid-crystal phase relations, upon which the internally self-consistent thermodynamic data are based, and difficulty in synthesizing the pure phases by repeated grinding and sintering of stoichiometric mixtures of oxides. Impurities visible only by SEM may have compromised literature calorimetric data. Also, small adjustments to the relative solar system abundances of O, C and H have significant effects on the amount of free oxygen available for condensates, and may affect the relative stabilities of phases with different oxygen/cation ratios. Many refractory inclusions in CM chondrites are composed of hibonite and spinel with no melilite, which is predicted to condense at a temperature intermediate between the other two. This has been attributed to a higher rate of reaction of hibonite with the gas to form spinel than to form melilite, but the aluminate precursor of the melilite is uncertain due to uncertainties in thermodynamic data and elemental abundances. (2) Types A and B inclusions in CV3 chondrites contain primary spinel, melilite, Ca-, Al-rich clinopyroxene (fassaite) and, in Bs only, anorthite. They are igneous objects that probably formed by melting of pre-existing solid condensate assemblages. The fassaite has $\text{Ti}^{3+}/\text{Ti}^{4+} \sim 0.3-2$, and has been synthesized at 1500K and $\log f_{\text{O}_2} \sim \text{IW}-8$ by crystallization from a melt of Type B inclusion composition. This is very close to the f_{O_2} of a solar gas, making such inclusions the only objects known to have formed in a system of solar composition. It is not known if the diopside predicted to condense directly from the solar nebular gas would have the Al, Ti^{3+} or Ti^{4+} contents of the fassaite in the inclusions. To find out will require determination of Gibbs free

energies of formation for $\text{CaTi}^{4+}\text{Al}_2\text{O}_6$ and $\text{CaTi}^{3+}\text{AlSiO}_6$ as well as of the non-ideal solid solution properties of the latter components with diopside and Ca-Tschermak's pyroxene.

Liquid Condensates: The condensation T of a phase increases when the partial pressures of its constituents are increased, either by increasing the total gas pressure or by increasing the relative abundances of its constituents in the gas by, for example, vaporizing dust-enriched regions. If the total pressure or degree of dust enrichment are increased sufficiently, the pure phase would condense above the solidus T of a multicomponent liquid in which it is soluble, leading instead to direct nebular condensation of liquid. Under most conditions, compositions of the highest-T liquids lie in the $\text{CaO-MgO-Al}_2\text{O}_3\text{-SiO}_2\text{-TiO}_2$ (CMAST) system, free of alkalis and FeO, so have to be treated with Berman's CMAS liquid model, rather than with the MELTS model. Liquid-solid equilibration Ts predicted by the CMAS model are in error by $50\text{-}100\text{K}$ when the solids are intermediate members of solid solution series. The CMAS model should be expanded to include Ti and should be recalibrated with melilite and pyroxene solid solutions. At lower T, where high concentrations of FeO and alkalis would condense into these liquids, the MELTS model can be used, but there is no accurate thermodynamic model for transitional liquids, CMAS with low FeO and alkali contents.

Oxidation State of Chondrites: The $\text{FeO}/(\text{FeO}+\text{MgO})$ of olivine in ordinary chondrites, $0.01\text{-}0.30$, requires equilibration with a gas having $\log f_{\text{O}_2} \sim \text{IW}-1.5$, $\sim 10^5\times$ higher than that of a solar gas. To generate cosmic gases oxidizing enough to stabilize significant FeO in olivine at Ts above where Fe-Mg interdiffusion in olivine ceases, two classes of models have been proposed, enrichment in (a) dust or (b) water. In (a), the dust is enriched in O compared to H and C relative to the gas, and is concentrated relative to the gas by dynamic processes, whereupon the entire region is vaporized. In (b), water ice is slowly vaporized in the hot, inner nebula from bodies that migrate there from cold outer regions. The maximum f_{O_2} enhancement expected for large nebular regions is $30\text{-}1000\times$ too low in (a) and (b). Completely new ideas are needed.