Ge 212 Problem Set 5

Due Friday November 10, 2017

Note: Use a computer for problems where it seems appropriate.

1. The following measurements give the density of a binary solution at ten compositions expressed as X, the weight fraction of component B, ranging from pure component A (*X* = 0) to pure component B (*X* = 1).

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| *X* (by weight) |  (g/cm3) |
| 0 | 5.000 |
| 0.1 | 7.273 |
| 0.2 | 7.692 |
| 0.3 | 6.154 |
| 0.4 | 4.545 |
| 0.5 | 3.478 |
| 0.6 | 2.857 |
| 0.7 | 2.548 |
| 0.8 | 2.500 |
| 0.9 | 2.797 |
| 1 | 4.000 |

1. Make a graph of specific volume  vs. *X* (specific volume = 1/).
2. Using a numerical approximation to  (and I recommend centered difference except at the endpoints), obtain estimates for the partial specific volumes of components A and B and the apparent specific volume of B at each of the measured compositions. Add these three curves to your plot from (a).
3. The method in (b) is not very accurate for such sparsely spaced data, especially near the end-points. So, redo it but this time fit a polynomial to the volume data (what degree of polynomial seems to be necessary?), and then differentiate the polynomial curve to get the partial specific volumes of A and B and the apparent specific volume of B (including in the limit X = 0). Redo the graph.
4. Do you get regions where  is concave-up and others where it is concave-down? Is that OK for a stable phase?
5. Do you get places where either the partial specific volume of A or B or the apparent specific volume of B is negative? Is that OK for a stable phase?
6. (Everything in this problem at 1 bar) The difference in evolved heat between (i) dropping a mole of andalusite (Al2SiO5) at 968 K into a solution calorimeter at 968 K and (ii) dropping one mole of corundum (Al2O3) at 968 K and one mole of quartz (SiO2) at 968 K into the same solution calorimeter at 968 K is –8.32 kJ. Hence for the reaction corundum + quartz = andalusite, r*H*(968 K) = –8.32 kJ/mol. Given the following heat capacity functions

*Cp*(*T*) = k0 + k1*T*–0.5 + k2*T*–2 + k3*T*–3 J/mol/K

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| Phase | k0 | k1 | k2 | k3 |
| corundum | 155.02 | –828.4 | –38.614x105 | 40.908x107 |
| quartz | 80.01 | –240.3 | –35.467x105 | 49.157x107 |
| andalusite | 236.48 | –1102.9 | –75.268x105 | 93.644x107 |

1. calculate r*H* (298.15 K) for the formation of andalusite from its oxides at 298.15 K (ignore, for today, the - quartz transition).
2. f*H*corundum(298.15 K) = –1675.7 kJ/mol and f*H*quartz(298.15 K) = –910.7 kJ/mol. Given those values, calculate f*H*andalusite(298.15 K), i.e. the enthalpy of formation of andalusite from the elements at 298.15 K.
3. With a few additional facts, you can (actually, you will…) calculate the pressure of the univariant equilibrium curve corundum + quartz = andalusite from 500 to 2000 K. Use either the direct method (at each *T*, solve for the *P* where fGandalusite = fGcorundum +fGquartz) or the indirect method (solve one such point, then integrate the Clausius-Clapeyron equation dT/dP = rV/rS). Additional facts: Scorundum(298.15 K) = 50.820 J/mol/K, Squartz(298.15 K) = 41.46 J/mol/K, Sandalusite(298.15 K) = 91.434 J/mol/K.
   1. Take the volumes of the phases to be constants: Vocorundum = 25.58 cm3/mol, Voquartz = 22.69 cm3/mol, Voandalusite = 51.47 cm3/mol.
   2. Now try again using these volume functions and see how different the result is:

V(*P,T*)/Vo = 1 + v1(*P* – 1) + v2(*P* – 1)2 + v3(*T*–298.15) + v4(*T*–298.15)2

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| Phase | v1 | v2 | v3 | v4 |
| corundum | –0.385x10–6 | 0.375x10–12 | 21.342x10–6 | 47.180x10–10 |
| quartz | –2.434x10–6 | 10.137x10-12 | 23.895x10–6 | 0 |
| andalusite | –0.770x10–6 | 1.923x10–12 | 23.443x10–6 | 7.189x10–10 |