

### Homework 3 Advanced Thermodynamics Due Monday September 13, 2021

Single component systems display first order transitions characterized by two phases being at equilibrium.

- a) Sketch the isochoric PT diagram for water showing the liquid, vapor, and solid regions, the triple point and the critical point. Explain how the Gibbs phase rule accounts for the triple point, the phase boundaries and the regions that contain a single phase.
- b) Sketch the isothermal PV phase diagram for water. Indicate the two-phase region, and the critical point. Can you show the triple point on this phase diagram? What happens when the specific volume is  $200 \text{ cm}^3/\text{mole}$  and the pressure is 10 MPa? (Explain how a tie-line works.)
- c) Use the PREOS.xls excel sheet to calculate the equilibrium boiling point of water at 1 MPa. First go to the Props tab and replace the name,  $T_c$ ,  $P_c$  and  $\omega$  values from the crit. Props tab for water, copy the ABCD values from the IG Cps tab for water to the Props tab. Go to the Ref State tab and choose 2 below the red text. This is the phase with the lowest fugacity (chemical potential) which is liquid water (lowest specific volume). Go back to the Props tab. Under Tools/Protection choose “unprotect sheet”. This is necessary to use solver. Set the pressure to 1 MPa. Make sure you have values for fugacity for the vapor (high specific volume) and liquid (low specific volume). At 298K you should. Go to Tools and choose “solver”. Set the target cell to be the “fugratio”. This is the fugacity ratio for liquid and vapor phases. You want this to be equal to 1 so set the next box to 1. By varying Temperature so choose the blue temperature of the current state (NOT THE  $T_c$  value!!!). Run solver and it should find the temperature where at 1 MPa (10 bar) the liquid and vapor are at equilibrium. What is the density (1/specific volume) for a 50/50 molar mixture of liquid and vapor under this condition?
- d) Download the Thermocalc program from the link on the webpage. (You can also use OPEN CALPHAD on a PC). If you use Thermocalc follow the procedure on the webpage [https://www.youtube.com/watch?v=hbhWAUwydDg&feature=emb\\_rel\\_end](https://www.youtube.com/watch?v=hbhWAUwydDg&feature=emb_rel_end) to determine the carbon iron phase diagram at 1 bar. Make a plot from 0 to 10 percent carbon with increments of 1 percent for 500 to 3000°C. Recalculate the phase diagram at 10 bar and compare the two phase diagrams.
- e) The van der Waals model for single phase systems includes a parameter “b” which is the excluded volume. Excluded volume can be important to determining the electrical conductivity of a carbon nanotube nanocomposite. Ayagara AR, Langlet A, Gratton M, Hocine NA *Prediction of the piezo-resistive behavior of rubber/carbon nanotube nanocomposites under quasi-static compression* Composites A 147 106428 (2021) estimate the excluded volume for nanotubes using equation 6. Explain the origin of this equation and how the excluded volume could be used to estimate the conductivity of a nanocomposite.