3.020, Spring 2021
Thermodynamics of Materials
Problem Set 8

Massachusetts Institute of Technology
Department of Materials Science and Engineering

Due April 30, 2021 at 10am EDT

We encourage you to work in groups. If you do so, please note the names of your groupmates on the first page of your solutions.

Remember to clearly present your solutions, including intermediate steps. Failure to show your work may result in reduced credit. Sloppy presentation may result in reduced credit.

Thermo 8.1: Reverse engineering a binary phase diagram, part I [30 pts]

In this problem you will study the Ti-Zr system. You will use Thermo-Calc to explore the binary phase diagram. Then, you will build thermodynamic models needed to re-create the phase diagram -- this is akin to reverse-engineering Thermo-Calc. In problem 8.2 (below), you will simulate your reverse-engineered model.

(a) [3 pts] Using Thermo-Calc, plot the Ti-Zr binary phase diagram, which is available within the Copper Demo Database v 1.0. Here and throughout, use Zr mole fraction (X_{Zr}) as your composition variable. Hand in a printed diagram with all phases and two-phase regions labeled.

Note: Due to an irregularity in Thermo-Calc, this problem is best done if you keep only the three relevant phases selected: BCC_B2, HCP_A3, and LIQUID

(b) [8 pts] Write down a full set of thermodynamic models and parameters that would be sufficient to re-create a phase diagram.

You can model each of the three phases as simple regular solutions. You can model the heat capacity of each pure phase as a linear function of temperature, which is a good approximation in a vicinity of the melting temperature.

In this step, we are not asking you for the actual data, *i.e.* the numerical values. Instead, we are asking you to define a system of models and parameters that could completely the phase diagram. You will find the actual data in the next step.

(c) [12 pts] Use Thermo-Calc to determine numerical values for the models for pure Ti and pure Zr that you defined above in (b). For each model, hand in a plot showing both the data and your model. State which data analysis software you use to fit the data (*e.g.* Excel, Matlab, Mathematica).

Thermo-Calc does not display heat capacity (c_P), but it does provide enthalpy (H). As you know, c_P and H are related by the differential equation

$$\frac{dH}{dT}\bigg|_P = c_P$$

Therefore, if c_P is a linear function of temperature, then H is a quadratic function of temperature:

$$c_P = a + bT$$
$$H = \frac{b}{2}T^2 + aT + +H_0$$

H_0 is an integration constant. The parameters a and b in the heat capacity model can therefore be determined from a quadratic fit to $H(T)$.

Below is an illustration of this analysis for HCP Zr. We exported the enthalpy data for pure Zr and plotted it in Matlab. We then fit the data to a 2nd order polynomial, limiting the temperature range of the fit to that within which the HCP phase is stable:
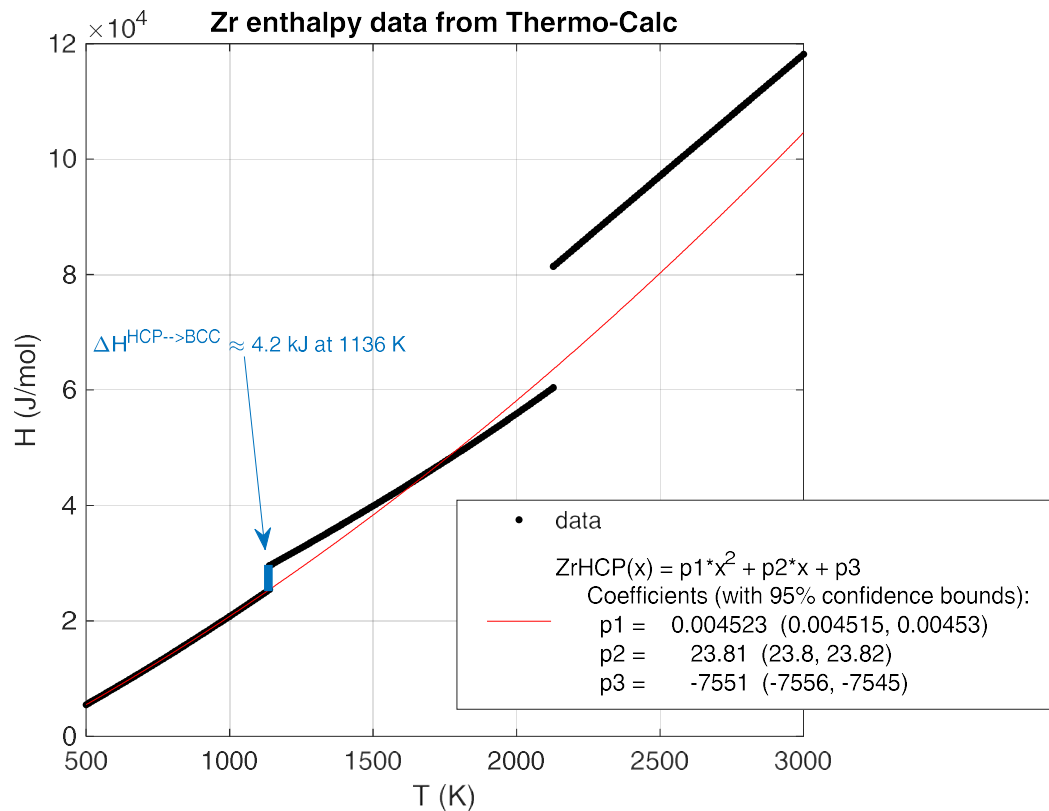
We determine the heat capacity model parameters from the polynomial coefficients, which Matlab lists as p1, p2, p3:

$$b_{Zr}^{HCP} = 2 \times p1 = 0.00905 \text{ J/K}^2, \qquad a_{Zr}^{HCP} = p2 = 23.8 \text{ J/K}$$

With the heat capacity of HCP Zr determined, you still need to determine the heat capacity model for the 5 remaining phases. After you do it once, the rest should go quickly, but it still may be tedious. If you like, you can show your work for one case, and borrow the work of others for the remaining cases (*e.g.* a team of 5 people, one to tackle each model). If you lean on others, please list your teammates on your problem set.

Thermo-Calc can be compelled to output heat capacity directly, using macros. You are most welcome to explore this route – you will become a Thermo-Calc power user in the process – but for most students, it will be fastest to extract the enthalpy data from Thermo-Calc and analyze it elsewhere as described above.

For the phase transformation quantities, you can eyeball the values from plots in Thermo-Calc or elsewhere – above we've eyeballed the transformation quantities for the HCP →

BCC transformation in pure Zr. In this case, we determined the numbers by mousing over the plot in Thermo-Calc and recording the data.

Points will be awarded based on reasonableness of your answers, but not on the quantitative values. It is not worth your time to strive for precision at this step - we are looking for common sense.

(d) [7 pts] Determine numerical values and validity of the solution models that you defined above in (b).

The enthalpy of mixing in the simple regular solution model has one adjustable parameter (a_0 in DeHoff). Optimize this parameter for each of your three solution models using enthalpy data from Thermo-Calc. Hand in a plot showing both the data and the fitted model, plus a comment on the apparent validity of the model. State which data analysis software you use to fit models and plot data (*e.g.* Excel, Matlab, Mathematica).

If any of the phases might be reasonably modeled as an ideal solution, then please state and justify this. In such cases, there are no adjustable parameters to determine.

Points will be awarded based on reasonableness of your answers, but not on the quantitative values. It is not worth your time to strive for precision.

~~Thermo 8.2: Reverse engineering a binary phase diagram, part II [7 pts]~~

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