Homework 7

Exercise 1. Baroplastics

Baroplastic materials are transformed from solid state to liquid state under the application of pressure at reasonably low temperatures. With this property, a plastic material can be molded into different shapes with the help of pressure. This new class of materials has been proposed to replace traditional thermoplastic materials for their low-temperature and low-pressure processing, and faster production. These materials are mainly investigated as a future avenue for recyclable polymers. The goal would be to recycle polymer waste by applying pressure at room temperature and thereby achieving a liquid that can be further processed. In this problem, we will consider a baroplastic material as a pure substance.

- a) Based on the provided information, what does a pressure-temperature (p-T) phase diagram of a typical baroplastic material look like? Make sure to label regions of the 3 phases (solid, liquid, vapor).
- b) Do you know of any material (not a baroplastic) that has a similar phase diagram?
- c) Indicate in the diagram the degrees of freedom according to the phase rule.
- d) Indicate on the phase diagram that you have drawn, what is the key phase line that matters for a baroplastic. Please explain what the relationship between the slope of the phase line and the performance of the materials is. Specifically explain how that phase line is related to the optimization of the baroplastic material to potentially reduce the molding cost.
- e) Indicate in your diagram where the atmospheric temperature and pressure are. Explain where it should be for an ideal baroplastic material to be useful in practice.

For the second part of this exercise, we shall consider hypothetical experimental measurements for a candidate baroplastic and try to understand it thermodynamically.

f) Assume that a group of researchers has reported the following relations for the slopes of a p-T diagram for a new baroplastic material.

$$0 < \left(\frac{dp}{dT}\right)_{sublimation} < \left(-\frac{dp}{dT}\right)_{fusion} < \left(\frac{dp}{dT}\right)_{vaporization} (1)$$

Draw the p-T phase diagram with the given properties.

- g) What is the key difference between the phase diagram in the previous part and your new phase diagram?
- h) Given the second phase diagram that you have drawn, please derive a relationship between the experimental results in eq. (1) and the molar entropies of the three phases of the materials that the researchers have discovered.
- i) What is the most unusual property? Do you think that this material is possible or that the researchers made a mistake in determining their phase diagram?