3.020, Spring 2021
Thermodynamics of Materials
Problem Set 5

Massachusetts Institute of Technology
Department of Materials Science and Engineering

Due April 2, 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 5.1: Solutions all around you [5 pts]

Identify two solid solutions that are essential for your daily life and/or modern technology. In each case, describe:

(a) The material and where it's found

(b) A typical composition

(c) The dominant atomic/molecular structure

(d) One important physical property that justifies its use

(e) The ways in which this key property differs in the solution from that of the pure components - that is, why is the solution superior than the unmixed pure components.

Thermo 5.2: Gibbs-Duhem [5 pts]

For an ideal solution $\Delta\overline{G}_2 = RT \ln X_2$. Use Gibbs-Duhem integration to derive the corresponding relation for component 1.

Thermo 5.3: There's always a solution! [5 pts]

Consider a binary system that obeys a simple regular solution model:

$$\Delta G_{\text{mix}} = aX_1X_2 + RT \sum_{i=1}^{2} X_i \ln X_i \tag{1}$$

Justify why that equilibrium at finite temperature will always involve a finite amount of mixing. That is, even for a large and positive a, there will still be an infinitesimal solubility of one component in the nearly-pure phase of the other. *Note: The reason is the same for why, in a reacting ideal gas mixture, the reaction at equilibrium is never fully complete.*

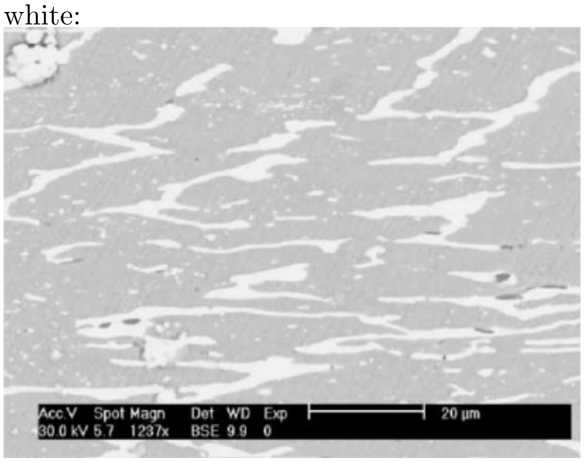
Thermo 5.4: Henry and Raoult, BFFs [5 pts]

Use a Gibbs-Duhem integration to prove that Raoult's law of the solvent implies Henry's law of the solute.

Thermo 5.5: Exploring the Ag-Cu system, part I [10 pts]

The silver-copper system historically played an important role in both art and currency. Silver is largely extracted from copper ores, and old silver currency usually has retained an appreciable amount of copper (for example, "Britannia silver" is an old English standard permitting no more than about 4% copper). Artisans have also deliberately alloyed silver and copper for aesthetic (as in Japanese "Shibuichi") and mechanical (as in "sterling silver") reasons; pure silver is very soft, but a copper-silver alloy is strong enough to resist wear in everyday objects. In modern times, silver-copper alloys are important as high-conductivity electronic solder.

The silver-copper system features two stable solid-solution phases: Ag(ss) and Cu(ss). A micrograph of a Cu-Ag alloy is shown below - a Gallo-Roman coin with Cu(ss) in grey and Ag(ss) in white:



Deraisme et al., Archaeometry 48:3 (2006)

(a) [3 pts] Use Thermo-Calc to generate the Ag-Cu phase diagram. Use "Solder Demo Database" as your data source. Use the mole fraction of Cu as the x-axis of the phase diagram, and temperature between 500 - 1400 K as the y-axis. Label the points, lines, and regions of the phase diagram. Submit your labeled phase diagram.

(b) [3 pts] Generate a plot of the Gibbs free energy of the system in the Cu(ss) phase at 1050 K for $X_{\text{Ag}} = 0 - 0.05$

(c) [4 pts] The molar Gibbs free energy of mixing of the Cu(ss) phase at 1 atm can be modeled as:

$$\Delta G_{\text{mix}} = a_0 X_{\text{Ag}} X_{\text{Cu}} + RT\left(X_{\text{Ag}} \ln X_{\text{Ag}} + X_{\text{Cu}} \ln X_{\text{Cu}}\right)$$

Extract the data from your plot from part (b), and import it into a data analysis software of your choice. Use linear regression (*i.e.* polynomial curve fitting) to determine a_0. Submit your estimate of a_0, the polynomial expression that you used for curve fitting, and a plot of the data together with the best-fit curve.