

# 3.020, Spring 2021

## Thermodynamics of Materials

### Problem Set 10

*Massachusetts Institute of Technology*  
*Department of Materials Science and Engineering*

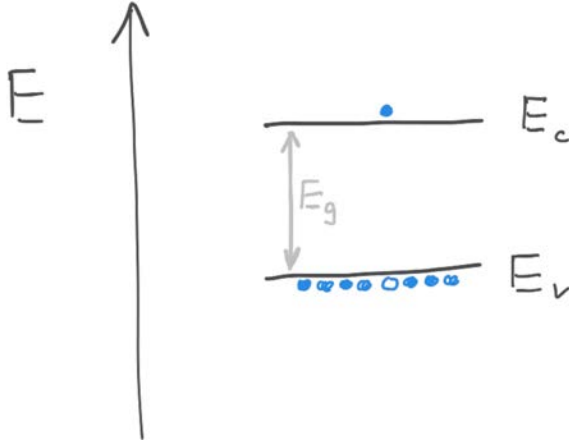
Due Friday May 14, 2021 at 10am EDT

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 10.1: Energy levels in a semiconductor [7 pts]

Electronic materials (metals, semiconductors, dielectrics) can be described by the distribution of states that may be occupied by electrons. Semiconductors have a gap in this distribution as a function of energy - a window in energy within which there are no available electronic states. This is known as the band gap, of width  $E_g$ . The collection of single-electron states immediately below the band gap is called the valence band, and the collection immediately above is called the conduction band. Here is a schematic with electrons represented as blue circles. In this picture, one electron has been excited from the valence to the conduction band, leaving behind an empty state (known as a "hole").



- (a) [3 pts] Silicon has a band gap  $E_g = 1.1$  eV. How much less likely is it for an electron to occupy a state in the conduction band than a state in the valence band at 300 K? At 400 K? At 1000 K?
- (b) [2 pts] In a laser, electrons are pumped from the conduction to the valence band, and then emit a photon as they relax back to the valence band. The pumping mechanism can be optical (as in a dye laser) or electrical (as in a solid-state laser diode). If the pump is sufficiently strong, the system can have more electrons in the high-energy state than in the low-energy state - this is known as population inversion. Consider silicon in a state of population inversion, in which a given state in the conduction band is 1% more likely to be occupied than a given state in the valence band. What is the apparent temperature of this system? *Hint*: Expect a wacky answer.
- (c) [2 pts] In the above you considered a system out-of-equilibrium, with a wacky apparent temperature. When a laser loses energy by emitting light, the energy is transferred to the surroundings partly in the form of work. This is as opposed to non-laser light emitters, such as the Sun or a common light bulb, that transmit light energy in the form of heat. You will hopefully study this one day in more advanced courses in thermodynamics and semiconductors. Provide another example of a physical system that can be driven/pumped out-of-equilibrium, and then can perform useful work as it relaxes back to equilibrium.

## Thermo 10.2: Doping semiconductors [15 pts]

Without control of chemical doping there would be no semiconductor technology - it's that important. In this problem we will consider the equilibrium concentration of metal dopants in silicon

(Si). Most metals are insoluble in Si. For instance, of the transition metals, Cu is the most soluble in Si. At 1100 °C, the solubility limit of Cu in Si is  $8 \times 10^{17} \text{ cm}^{-3}$ . Since the atomic density of Si is  $5 \times 10^{22} \text{ cm}^{-3}$ , this means that the solubility limit of Cu is 16 ppm. On the Cu-Si binary phase diagram, Si appears as a line compound (look it up!).

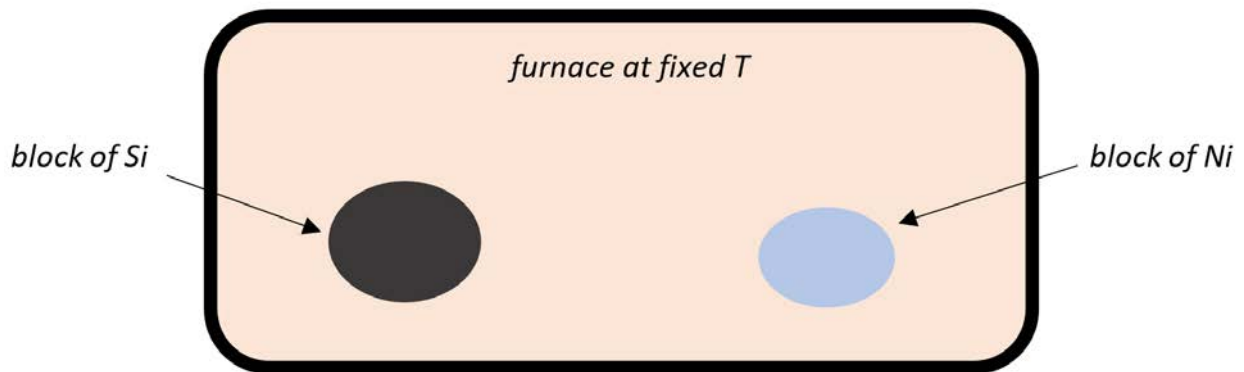
At such low concentrations, metal atoms in the Si lattice don't interact with each other. As a result, the enthalpy of introducing an individual defect is approximately a constant, independent of the number of point defects present - this means the dilute solution model applies. Specifically, we approximate that the enthalpy  $\Delta H_{\text{dope}}$  of the following reaction is linear in the amount  $\delta$  of metal (M) atoms moved into the Si lattice:



This enthalpy can be calculated using density functional theory (DFT) by considering moving a single metal atom from its elemental state into the semiconductor, and is often reported in units of eV/atom. Since this is relatively temperature-independent at temperatures much below the melting points of the solids, the zero-temperature ("ground state") value from DFT is often used. The entropy of the above reaction can be approximated as the ideal, configurational entropy of mixing:

$$\Delta S_{\text{dope}} = -R(\delta \ln \delta + (1 - \delta) \ln(1 - \delta)) \approx -R\delta \ln \delta \quad (\delta \ll 1)$$

In parts (a-b) you will consider Si in thermodynamic equilibrium with pure Ni, as in this cartoon:

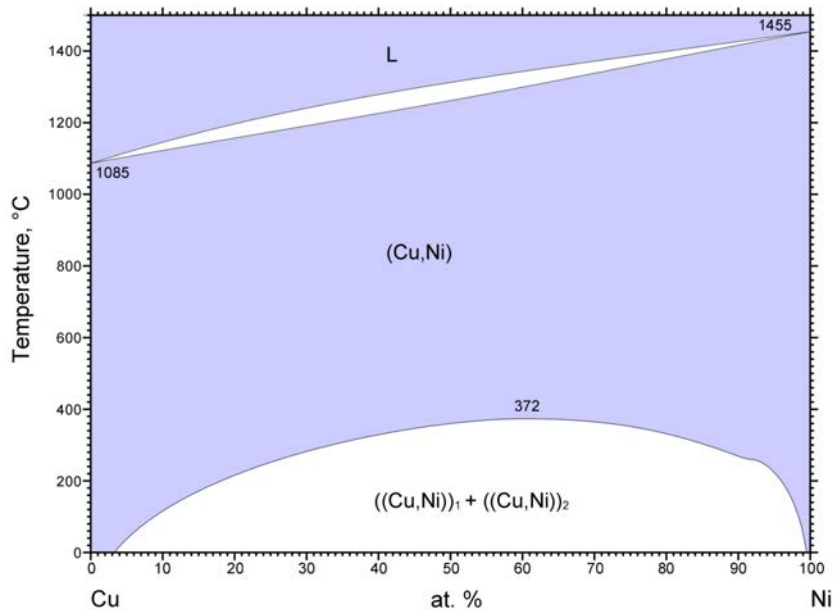


- (a) [5 pts] The enthalpy  $\Delta H_{\text{dope}}$  for introducing a single Ni interstitial in Si is 1.68 eV/atom. What is the equilibrium concentration (in  $\text{cm}^{-3}$ ) of Ni interstitials in Si at 800 °C? This quantity is often written  $[\text{Ni}_i]$ , where the subscript "i" stands for interstitials, and the square brackets indicate a concentration.

*Hint:* Consider the chemical potential change of Ni due to doping in Si,  $\Delta\mu_{\text{Ni}}^{\text{Si}}$ .

- (b) [2 pts] What is the equilibrium  $[\text{Ni}_i]$  in Si at room temperature?

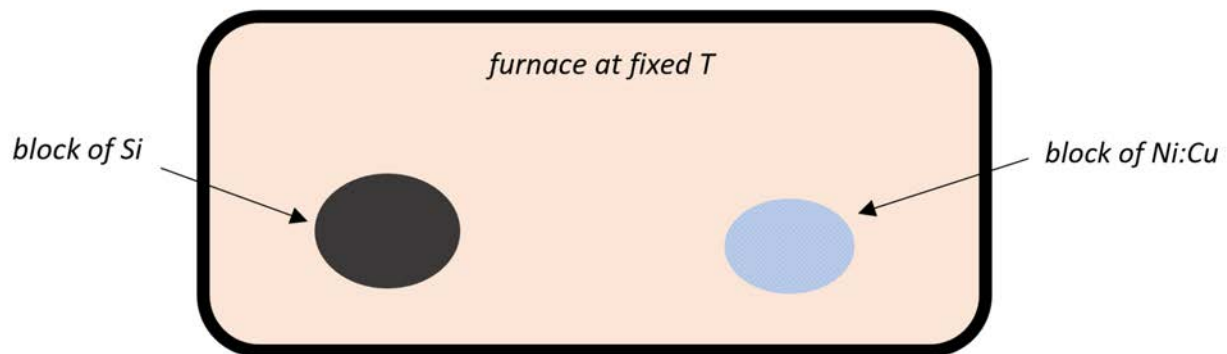
Parts (a-b) were about controlling the chemical potential of Ni ( $\mu_{\text{Ni}}$ ) with temperature. You know of another, powerful way to control  $\mu_{\text{Ni}}$  – with composition! Instead of pure Ni, consider using a (Ni,Cu) alloy. The Ni-Cu system is isomorphous with a low-temperature spinodal:



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This looks like it can be modeled using a regular solution model for the solid phase, with an endothermic enthalpy of mixing  $a_0$ .

- (c) [2 pts] The spinodal temperature is 372 °C. Estimate  $a_0$ , using your knowledge of the simple regular solution model. *Note:* The phase diagram doesn't look exactly like a simple-regular model, because the spinodal region is not symmetrical about  $X_{Ni} = 0.5$ . Please ignore this.
- (d) [4 pts] Consider a problem like in (a-b), but with a block of  $Ni_{1-x}Cu_x$  instead of pure Ni:



Write an expression for  $[Ni_i]$  as a function of  $T$  and the composition  $x$  of the  $Ni_{1-x}Cu_x$  piece, using your estimate for  $a_0$  from part (c).

- (e) [2 pts] What is the equilibrium concentration (in  $cm^{-3}$ ) of Ni interstitials in Si at 800 °C in this situation for a block of  $Ni_{0.99}Cu_{0.01}$ ?

### Thermo 10.3: Whatsit with Ellingham and Richard [8 pts]

You discovered a new element. Congratulations! From its appearance and electrical conductivity you infer that it's metallic. Not knowing anything else about it, you christen it Whatsinium (Wh). You find that it oxidizes rather easily, and that the oxide has the chemical formula  $\text{Wh}_2\text{O}_3$ .

- (a) [2 pt] What is the oxidation state of Wh in its oxide?
- (b) [3 pt] You find that the heat of oxidation of Wh is  $-652$  kJ per mole of Wh. List three metals that in their elemental form would likely reduce  $\text{Wh}_2\text{O}_3$  when mixed and heated at moderate temperatures.
- (c) [3 pt] Whatsinium turns out to be a rather strange system. You find that the oxide melts at  $920$  °C and boils at  $1000$  °C, while the metal doesn't melt until  $1900$  °C. Draw an Ellingham diagram for Wh (not including any other metals). Your diagram doesn't have to be accurate, but it should be qualitatively consistent with what you know so far.

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