3.020, Spring 2021
Thermodynamics of Materials
Problem Set 4

Massachusetts Institute of Technology
Department of Materials Science and Engineering

Due March 26, 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 4.1: Le Chatelier strikes again [12 pts]

(After Denbigh 9.6) Reacting gas mixtures are useful for regulating temperature. Consider a reacting mixture of N_2, H_2, and NH_3. Show that the effective molar heat capacity of this reacting mixture at equilibrium is higher than the heat capacity of the same quantities of pure gases, not allowed to react. In other words, show that the ability of the system to react increases its heat capacity. The effective heat capacity is the heat required to raise the temperature of the system at fixed pressure. You can assume 1 bar and 298 K. You can assume that the system behaves as a mixture of ideal gases. As always, cite your data sources.

Hint 1: You will need the van't Hoff equation.

Hint 2: You will need to find the standard enthalpy and Gibbs free energy of the ammonia synthesis reaction.

Thermo 4.2: Making CO [9 pts]

(Denbigh problem 9.9, reproduced here) At 1200 K, the equilibrium constants of the reactions

$$\mathrm{C(gr)} + \mathrm{CO_2} = 2\mathrm{CO}$$
$$\mathrm{CO_2} + \mathrm{H_2} = \mathrm{CO} + \mathrm{H_2O}$$

are 63 and 1.4, respectively (expressed for pressure in units of atmosphere). The standard free energy and enthalpy of formation of water vapor at 25°C are -54,640 and -57,800 cal/mol, respectively. Heat capacity data are as follows:

$$\mathrm{H_2} \quad c_P = 6.947 - 0.2 \times 10^{-3}T + 4.8 \times 10^{-7}T^2$$
$$\mathrm{O_2} \quad c_P = 6.148 + 3.1 \times 10^{-3}T - 9.2 \times 10^{-7}T^2$$
$$\mathrm{H_2O}(g) \quad c_P = 7.256 + 2.3 \times 10^{-3}T + 2.8 \times 10^{-7}T^2$$

Use this data to evaluate the equilibrium constant at 1200 K of the reaction:

$$\mathrm{C(gr)} + \frac{1}{2}\mathrm{O_2} = \mathrm{CO}$$

Thermo 4.3: Fixing nitrogen with Fritz Haber [9 pts]

The Haber process is one of the most important discoveries of all time, because it enabled industrial-scale production of ammonia for fertilizer. Friz Haber's life is an incredible story and a cautionary tale about personal ambition and the morality of science - I encourage you to read about his life, here is a good place to start:
https://www.smithsonianmag.com/history/fritz-habers-experiments-in-life-and-death-114161301/

You worked with the ammonia formation reaction in problem 4.1. As before, you can assume that all components behave as ideal gases.

(a) [4 pts] Assuming that the reaction chamber initially contains a stoichiometric mixture of H_2 and N_2: 3/2 mol of H_2 and 1/2 mol of N_2. Calculate the mole fraction of NH_3 for this reaction at equilibrium at 25 °C and 450 °C. You can assume that the total pressure in the reaction chamber is 1 atm, and that there are no other species present besides those in the above reaction. As before, cite your data sources.

(b) [4 pts] Assume that you start with the equilibrium mixture at 25 °C as described above. How much heat energy is required to raise the temperature of the reacting system to 450 °C?

(c) [1 pt] Explain in words why more ammonia production can be expected (the reaction will move to the right) with increasing pressure in terms of Le Chatelier's principle.