Thermodynamics (50 points total):

1. Consider a thermodynamic system consisting of 1 mole of the material examined in problem 3- (alumina, Al_2O_3)- in the solid state, reversibly heated at a constant pressure of 1 atm from 20°C to 200°C in an oven. Solid alumina is the stable phase throughout this temperature range. **Be sure to show your work in each part- this makes it possible to give partial credit**.

   Thermodynamic data for Al_2O_3:

$$C_P^s = 106.6 + 0.0178T - 28.5 \times 10^5 T^{-2} \quad \frac{J}{mole \cdot K}$$

   T_m = 2327 K

   Alumina has no structural phase transitions in the temperature range of interest.

   a. (4 points) What type of system is this? (State your assumptions.)

This is a closed system. Because the temperature of the system is being increased by heating, it clearly allows heat transfer. We assume here that we can neglect vaporization of the alumina (loss of molecules to the surroundings).

   b. (8 points) Determine the heat transferred to the system in this process.

The constant pressure heat capacity is defined as:

$$C_P^s = \left(\frac{dq_{rev}}{dT} \right)_P$$

Thus we can rearrange and integrate to determine the heat transfer occurring:

$$q_{rev} = \int_{293}^{473} C_P^s \, dT = \int_{293}^{473} \left(106.6 + 0.0178T - 28.5 \times 10^5 T^{-2} \right) dT$$

$$q_{rev} = \left(106.6T + \frac{0.0178}{2} T^2 + 28.5 \times 10^5 T^{-1} \right) \Big|_{293}^{473} = 16,713 \, J$$

c. (8 points) If the internal energy of the system increases by 33,500J in this process, what is the reversible work performed? Is this work **done on** the system or **done by** the system?

Most generally, the first law is:

$$dU = dq + dw$$

For the present constant pressure process, we can substitute:

$$w = \Delta U - q = 33,500 - 16,713 = 16,787 J$$

This is work done on the system during the process. As a side note, where might this work come from? Remember that the work of hydrostatic pressure is only the most common mechanical work to consider, but multiple forms of internal changes can occur in materials, such as chemical changes.

d. (8 points) What is the enthalpy change in the system during this process?

Because this process is performed at constant pressure, the enthalpy change is simply equal to the heat transfer:

$$dH = dU + VdP + PdV$$
$$dH = dq + VdP$$
$$dH\big|_P = dq$$
$$\therefore \Delta H = q = 27,253 J$$

e. (8 points) What is the entropy change in the system?

The entropy change can be determined by returning to an equality for the heat capacity:

$$C_P^s = \left(\frac{dq_{rev}}{dT}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$dS = \frac{C_P^s}{T}dT$$

$$\Delta S = \int_{293}^{473} \frac{C_P^s}{T} dT = \left(106.6\ln\left(\frac{473}{293}\right) + 0.0178(473 - 293) + \frac{28.5 \times 10^5}{2}\left(\frac{1}{473^2} - \frac{1}{293^2}\right)\right) = 44.02 \frac{J}{K}$$

f. (8 points) If the system is now returned to its initial pressure, temperature, and volume by a series of stepwise compression and cooling steps, what will the internal energy change for the total return process be? State why.

Because internal energy is a state function, its return to the initial state by any path will result in an equal but opposite change in the internal energy:

$$\Delta U_{return} = -\Delta U_{first\ process} = -33,500\,J$$

g. (6 points) Finally, consider 1 mole of a sample of *aluminum* (heat capacity given below), which receives the same quantity of heat (at constant pressure) that was transferred to the Al_2O_3 sample above. (Solid aluminum is stable up to 932K). Without performing a detailed calculation, state whether the Al sample will have the same final temperature as the alumina sample, a lower temperature, or a higher temperature. Explain why in one or two sentences.

$$C_P^s = 20.7 + 0.0124T\ \frac{J}{mole\cdot K}$$

We know that at constant pressure, the heat transfer is related to heat capacity by:

$$q_{rev} = \int_{293}^{T'} C_P^s\,dT$$

Because the heat capacity of Al is significantly less than that of alumina, its temperature will be raised **higher** than that of alumina for any given total amount of heat absorbed. Just looking at the leading term of the heat capacities of each, we would have:

$$q_{absorbed} \approx 20.7\,T_{final}^{Al}$$

$$vs.$$

$$q_{absorbed} \approx 106.6\,T_{final}^{Al_2O_3}$$