EXERCISE 5B: FREE EXPANSION AND ENTROPY OF MIXING

Objectives:

- Review how we derive **Maxwell relations**
- Compare examples of **irreversible** and **reversible** processes in thermodynamics
- Calculate the **entropy of mixing** between ideal gases

1. *Heat Capacity of a Gas of Diatomic Molecules* (continued from last time).

    a. Figure 1 shows the heat capacity C_V of a gas of H_2. Explain this graph as completely as possible. Label the values of the plateaus on the vertical scale.

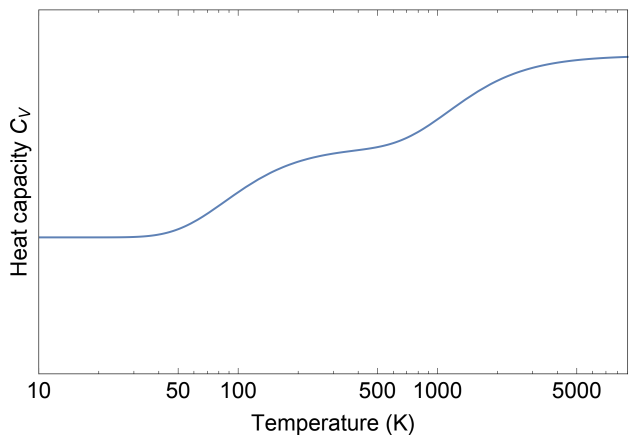

FIG. 1. Heat capacity of an H_2 molecule in the gas phase as a function of temperature T.

2. *A useful Maxwell relation for calculating changes in entropy.* Since the state functions τ, σ, p, V form an overcomplete description of a gas, you can derive a number of relations between them and their derivatives. Starting from the fundamental thermodynamic relation, derive a Maxwell relation of the form:

$$\left(\frac{\partial \sigma}{\partial V}\right)_\tau = \left(\frac{\partial A}{\partial B}\right)_V . \tag{1}$$

What are A and B?

3. *Sudden expansion of an ideal gas.* Consider an ideal gas initially confined in a volume V_i at temperature τ_1. We open a partition that allows the gas to expand to fill a volume $V_f = 2V_i$.

   a. How much work is done in the expansion? Explain.

   b. What is the temperature after the expansion? Explain.

   c. What is the change of entropy in the expansion? Let σ_i denote the entropy of the gas before the expansion and σ_f the entropy after expansion. Calculate $\sigma_f - \sigma_i$. *Hint:* Use the relation you found in problem 2.

d. Was the process we considered **quasistatic** or not? Was it **reversible** or **irreversible**?

e. How would you change the manner in which the gas is allowed to expand in order to change the (ir)reversibility of the process, compared with the case considered above?

4. *Entropy of mixing.* Two low-density gases of different species, each initially occupying a volume V_i and at the same temperature τ, are separated by a partition. The partition is punctured, allowing the gases to mix.

   a. Calculate the change in entropy $\sigma_f - \sigma_i$ resulting from the mixing of the two gases, assuming there are N_1 particles of species 1 and N_2 particles of species 2.

   b. Now suppose that the two species allowed to mix were the same. Would the change $\sigma_f - \sigma_i$ be the same or different from your result in a.? Explain.

c. *Gibbs paradox.* Suppose that two gases of N_1 and N_2 **distinguishable particles** are allowed to mix. What is the change in entropy in this case?

d. Which, if any, of the mixing processes considered above are **reversible**? Explain.

e. Are all of your results consistent with the fundamental thermodynamic relation? Explain.