

## Exercise Classes 2, Physical Chemistry 1 2021/2022

### Exercise 6

Consider 1.0 mol of a perfect gas of atoms at an initial temperature of 25 °C and a pressure of 5.0 bar.

- a) Calculate the following values for an isothermal and reversible expansion to a final pressure of 1.0 bar.
  - the final temperature of the gas,
  - the work done on the gas,
  - the increase in internal energy of the gas,
  - the heat absorbed by the gas,
  - the entropy change of the gas,
  - the change in the Helmholtz free energy of the gas and
  - the change in the Gibbs free energy of the gas.
- b) Find out (without calculation) for all quantities considered in the previous part of the exercise whether you expect a different answer for an isothermal expansion from  $P = 5$  bar to a final pressure of the gas of  $P = 1$  bar, but now against a constant external pressure of 1.0 bar. Note that this is an irreversible process.
- c) Then calculate the values from the first part for the irreversible process.

### Exercise 7

Consider an irreversible adiabatic expansion of  $n$  mol of a perfect gas in a cylinder sealed by a frictionless piston in vacuum. The piston is initially locked and when the lock is released, the piston can freely move. The initial pressure of the gas is  $P_1$  and the temperature is  $T_1$ .

- a) Determine the final temperature  $T_2$ .
- b) We determine the entropy change in terms of  $V_1$  and  $V_2$ .

Hint: Use the state function property of  $S$  and choose an alternative path consisting of a reversible isobaric and a reversible isochoric process.  
First sketch the three processes in a  $P - V$ -diagram.  
Then express  $\Delta S$  in terms of  $C_V$ ,  $C_P$  and the relevant temperatures using  $dQ = dH|_P = C_P dT$  and  $dQ = dU|_V = C_V dT$ .  
Finally you can use the perfect gas law to express  $\Delta S$  in terms of  $V_1$  and  $V_2$ .
- c) Find the conditions for which the process proceeds spontaneously.
- d) We conduct the experiment at  $T = 300$  K for 0.04 mol of gas with an initial volume of 1 L (corresponding to an initial pressure of  $P \approx 1$  bar) and a final volume of 2 L.  
Calculate the change in the Helmholtz and Gibbs free energy.

### Exercise 8

Consider the entropy change of a spontaneous process.

Two equal amounts of the same liquid are brought in contact with each other at constant pressure and without loss of heat (to the surroundings) via a heat permeable (thermal) wall, so without mixing the fluids. Note that we are not considering perfect gases, but liquids!

The initial temperatures of the liquids are  $T_1$  and  $T_2$  respectively, where  $T_1 < T_2$ . We assume that  $C_P$  of the liquids is constant between  $T_1$  and  $T_2$ . The final temperature  $T$  of both liquids will be equal.

Determine the entropy change during this process in terms of  $C_P$ ,  $T_1$  and  $T_2$ .

Use the second law of thermodynamics to show that this process proceeds spontaneously, as one would expect.