**Homework 3 Solutions**

1. Let's try to find the boundary conditions for the below cases. Consider a system consisting of a gas container with a freely moving piston at one end. State the type of process occurring (e.g. isothermal) for cases a. to c. below. You can assume that no leaks occur.
   a. The gas is quasistatically heated from T1 to T2 using a heating plate
   b. The freely moving piston is replaced with a rigid lid, and the gas is heated from T1 to T2 using a heating plate
   c. The lid is replaced with a piston once more. A hole is drilled in the container, and a tube is attached. Additional gas is reversibly transferred into the container through the tube at constant temperature.
   d. For case c. above, is the container system open or closed?

To understand which boundary condition we are setting, we need to identify which of the system's state variables we control for each case:

a. We control p (free piston), T (quasistatic heating), n (closed system), described by Gibbs potential G(T, p, n).

$$dG = SdT + V\underbrace{dp}_{0} + \mu\underbrace{dn}_{0}$$

→Boundary condition: Isobaric (dp=0), closed (dn=0).

b. We control V (rigid lid), T (heating), n (closed system), described by Helmholtz potential F(V, T, n).

$$dF = SdT + p\underbrace{dV}_{0} + \mu\underbrace{dn}_{0}$$

→ Boundary condition: Isochoric (dV=0), closed (dn=0).

c. We control p (free piston), T (fixed), n (reversible mass flux), described by Gibbs Free energy G(T, p, n). Mass transfer proceeds reversibly until **chemical equilibrium** is reached between gas and reservoir of gas particles.

$$dG = S\underbrace{dT}_{0} + V\underbrace{dp}_{0} + \mu dn$$

→ Boundary condition: Isobarothermic (dp=0 and dT=0).

d. Open, as matter is exchanged with the environment.

2. An ideal gas system undergoes isothermal expansion from an initial volume $V_i$ to a final volume $V_f$. What is the change in enthalpy of the system?

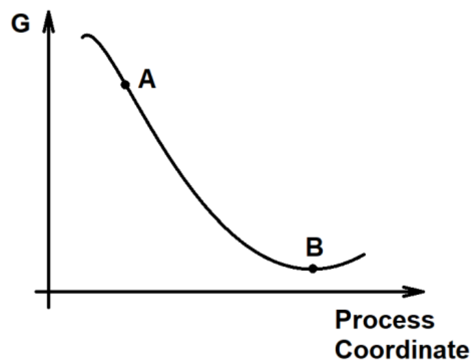
In a general case, enthalpy is defined as:

$H = U + pV$

For an ideal gas, the internal energy $U$ and $pV$ depend only on $T$ ($pV = nRT$ and, for example, $U = \frac{3}{2}nRT$ for a monoatomic ideal gas). Therefore, the enthalpy of the idea gas also depends solely on T. Hence, the change of enthalpy ΔH of an isothermal expansion from $V_i$ to $V_f$ is zero.

$H = U + pV = U + nRT \rightarrow \Delta H = 0$

3. For an arbitrary process in a closed system, a plot of the Gibbs free energy looks like this:




If the process is at the state **A**, is it possible for the system to spontaneously go to state **B**? Why or why not?

A spontaneous reaction means ΔG<0. Therefore, state **A** will spontaneously go to state **B**.

4. The heat capacity at constant volume $C_V$ of many solids at low temperature has the proportionality: $C_V = \alpha T^3$. What function describes the internal energy of such a material? Find the expression for the internal energy.

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V = \alpha T^3$$

Therefore the internal energy of this material at constant volume

$U = \int C_V dT = \frac{1}{4}\alpha T^4 + c$

5. In many thermodynamics' exercises a thermal bath is mentioned. Essentially, a thermal bath is an object or vessel, which can receive or give heat. We also consider it to be large enough so that it does not change its temperature. Usually water is used for such applications due to its large heat capacity. A copper piece (m = 10 g, $C_{Cu}$ = 0.385 J/g·K) that has initial temperature $T_{Cu}$ = 100 °C is dropped in a tank of water ($C_{H2O}$ = 4.184 J/g·K) with temperature $T_{H2O}$ = 25 °C. How much water is needed in the tank so the final equilibrium temperature of water and copper piece would be 25.1 °C? Note that in this exercise, we assume a constant heat capacity.

→ Because temperature is the variable we control, we can describe the internal energy as a function of temperature $dU(T) = mC_V dT$.

→ The copper and the water form a closed, isolated system that exchanges energy only through heat transfer (i.e. W=0), therefore, the total internal energy of the system remains constant.

$$U_{Cu} + U_{H2O} = const.$$
$$dU_{Cu} + dU_{H2O} = 0$$
$$dU_{Cu} = -dU_{H2O}$$
$$\int_i^f dU_{Cu} = \int_i^f dU_{H2O}$$

Since $\int_i^f dU = U(f) - U(i) = \Delta U$, we can write

$$\Delta U_{Cu} = \Delta U_{H2O}$$
$$m_{Cu}C_{Cu}(T_{Cu}^f - T_{Cu}^i) = -\, m_{H2O}C_{H2O}(T_{H2O}^f - T_{H2O}^i)$$

$$m_{H2O} = -\frac{m_{Cu}C_{Cu}(T_{Cu}^f - T_{Cu}^i)}{C_{H2O}(T_{H2O}^f - T_{H2O}^i)}$$

$$m_{H2O} = -\frac{10 \cdot 0.385 \cdot (25.1 - 100)}{4.184 \cdot (0.1)}$$

$$m_{H2O} = 689\ g$$

The large heat capacity of water leads to a situation where water can give and take a lot of heat and not change its temperature a lot. In many cases, a change of temperature during an experiment by 0.1 °C can be easily neglected and the water bath can be considered as a thermal bath.