

Thermodynamics. Problems. Sheet 2.

Solutions of the problems.

1. One mole of ideal gas expands isothermally from (P_1, V_1, T) to (P_2, V_2, T) in a single stage, against a constant opposing pressure equal to P_2 . If $P_1 = 10 \text{ atm}$, $P_2 = 5 \text{ atm}$ and $T = 300 \text{ K}$, what is the work done by the system? Represent the transformation in a P - V plane and indicate what the work is on the graph.

Since the opposing pressure (P_2) is constant the work is simply the product of this pressure times the volume change, $V_2 - V_1$. The problem is that we do not know these volumes. But we know it is an ideal gas, and we know the pressure and the number of moles:

$$V = \frac{NRT}{P}, \text{ where } R = 8.314 \text{ J K}^{-1}\text{mol}^{-1}, N = 1 \text{ mol}, T = 300 \text{ K}.$$

Therefore, using the equation of state of an ideal gas, we can compute V_1 and V_2 :

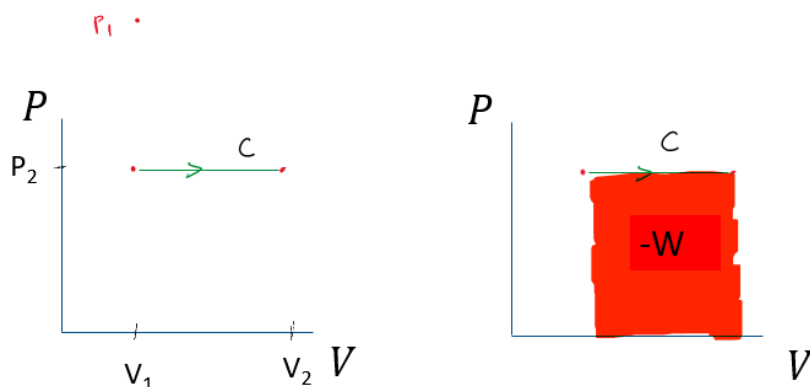
$$V_1 = \frac{NRT}{P_1} = \frac{1 \times 8.314 \times 300}{10 \times 101325} = 2.46 \times 10^{-3} \text{ m}^3$$

$$V_2 = \frac{NRT}{P_2} = \frac{1 \times 8.314 \times 300}{5 \times 101325} = 4.92 \times 10^{-3} \text{ m}^3$$

Therefore, the work is:

$$W = -P_2(V_2 - V_1) = -5 \times 101325 (4.92 - 2.46) \times 10^{-3} = 1247 \approx -1.25 \times 10^3 \text{ J}$$

Drawing:



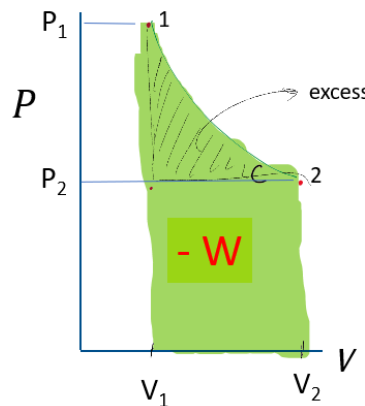
Note on significant digits: The problem statement does not specify the number of significant digits that are relevant to the computation. However, the numbers provided suggest that the accuracy is not better (perhaps worse) than 1 unit in 300 on the temperature. Therefore, three significant digits is required.

2. The same isothermal expansion of the previous problem is carried out, but in a reversible way (infinite stages). What is now the work produced by the system? Represent it graphically in a P-V plane.

The work is not reversible. Therefore, $dW = -P_{ext}dV = -P(V, T)dV$, and integrating between V_1 and V_2 .

$$W = - \int_{V_1}^{V_2} dV P(V, T) = - \int_{V_1}^{V_2} dV \frac{NRT}{V} = -NRT \ln \frac{V_2}{V_1} = -1 \times 8.314 \times 300 \times \ln \frac{4.92}{2.46} = -1.73 \times 10^3 \text{ J}$$

Drawing:



3. Write the reversible work of isothermal expansion of a van der Waals gas.

The van der Waals equation of state says:

$$P(V, T) = \frac{NRT}{V - bN} - a \left(\frac{N}{V} \right)^2$$

The reversible work is written as:

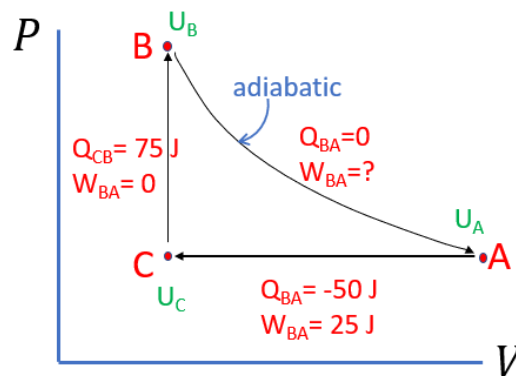
$$W = - \int_{V_1}^{V_2} dV P(V, T) = - \int_{V_1}^{V_2} dV \left[\frac{NRT}{V - bN} - a \left(\frac{N}{V} \right)^2 \right] = -NRT \ln \left(\frac{V_2 - bN}{V_1 - bN} \right) + aN^2 \left(\frac{1}{V_1} - \frac{1}{V_2} \right)$$

Note that the two addends work in opposite ways: If, for example, the final volume is greater than the initial volume (expansion), the first addend is negative, as expected, as energy is transferred from the system to the surroundings during an expansion. However, the second addend (although a correction) is positive.

4. A system consists of a gas contained in a cylinder closed by a piston. The system undergoes the following transformations:
- a) **A→C**: a volume reduction at constant pressure, during which it receives 25 J of work and gives up 50 J of heat to the environment.
 - b) **C→B**: a constant volume pressure rise during which it receives 75 J of heat.
 - c) **B→A**: returns to state A through an adiabatic transformation.

Represent the process by means of a P-V diagram and calculate the amount of work exchanged with the medium during stage c).

The process is cyclic (returns to the initial point). The cycle can be represented graphically in a P-V diagram as follows, where we have indicated the amounts of heat and work entering or exiting the system, using the convention of the signs (positive if it increases the internal energy).



The net change in the internal energy in the cycle is zero: $\Delta U = 0$. Therefore,

$$\begin{aligned}\Delta U = 0 &= \sum Q + \sum W = Q_{AC} + Q_{CB} + Q_{BA} + W_{AC} + W_{CB} + W_{BA} \\ &= -50 + 75 + 0 + 25 + 0 + W_{BA}\end{aligned}$$

Therefore, $W_{BA} = -50 \text{ J}$. The system does work (instead of receiving), as expected, since its volume is increasing.

Note also that the internal energies are in this order: $U_B > U_A > U_C$.

5. Liquid water, at 0°C and atmospheric pressure, has a density of 1,000 g cm⁻³. Under the same conditions, ice has a density of 0.917 g cm⁻³. How much work does 1 kg of ice do when it melts under these conditions?

The work is done against a constant pressure ambient. Therefore, the work is simply:

$$W = -P_a(V_f - V_i)$$

P_a is “atmospheric pressure”, which in absence of other information, we should take to be 1 atm, thus 101325 Pa. The volumes need to be computed from the mass and the densities:

$$V_i = \frac{M_i}{\rho_i}; V_f = \frac{M_f}{\rho_f}$$

$$W = -P_a \left(\frac{M_f}{\rho_f} - \frac{M_i}{\rho_i} \right) = -P_a M \left(\frac{1}{\rho_f} - \frac{1}{\rho_i} \right)$$

$$\rho_i = 0.917 \text{ g cm}^{-3} = 917 \text{ Kg m}^{-3}$$

$$\rho_f = 1,000 \text{ g cm}^{-3} = 1000 \text{ Kg m}^{-3}$$

$$M = 1 \text{ Kg}$$

$$P_a = 101325 \text{ Pa}$$

$$W = -P_a M \left(\frac{1}{\rho_f} - \frac{1}{\rho_i} \right) = -101325 \times 1 \times \left(\frac{1}{1000} - \frac{1}{917} \right) = \mathbf{9.17 \text{ J}}$$

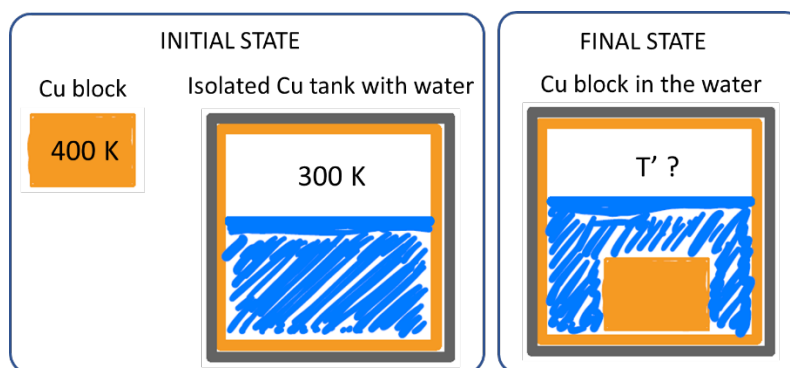
The work is positive, as the system lowers its volume (increases its density) during the process of melting. Therefore, it gains energy by work. However, note its internal energy increases during melting mainly due to the supply of the latent heat necessary for the melting. This amount greatly exceeds the work.

6. A copper block weighs 0.2 kg and has an initial temperature of 400 K. A perfectly insulated copper tank weighing 0.5 kg contains 4 kg of water, initially at 300 K. The copper block is immersed in the water and equilibrium is allowed to settle. What is the change in the internal energy of the copper block and the water? What is the change in energy of the entire system, including the tank? Ignore the effects of expansion and contraction and assume that the specific heats are constant and equal to $4.184 \text{ J g}^{-1} \text{ K}^{-1}$ for water and $0.380 \text{ J g}^{-1} \text{ K}^{-1}$ for copper.

This is a problem of calorimetry. Calorimetry problems are typically concerned with the exchange of heat from one body to its surroundings.

Our system is composed of two systems: The Cu block and the water/Cu-tank set.

The initial state of the system is these two separate subsystems with each one at a different initial temperature. The final state of the system is the two subsystems together at the same final temperature T' , unknown.



Since we are dealing with condensed matter, the work done by expansion or contraction during the temperature change of the materials is neglected. The subsystems exchange energy only through heat. The net change in energy of the entire system including the tank is zero (answer to the second question). The change in the internal energy of each component is as follows, where we use the following subscripts for each component: B for the Cu block, T for the tank, W for the water, Cu for copper (used for the specific heat); and refer to the initial temperatures as T (with sub-indexes):

$$\Delta U = \Delta U_B + \Delta U_T + \Delta U_W = 0$$

$$\Delta U_B = c_{Cu} M_B (T' - T_B)$$

$$\Delta U_T = c_{Cu} M_T (T' - T_T)$$

$$\Delta U_W = c_W M_W (T' - T_W)$$

Substituting the data into these, give us one equation with one unknown, T' :

$$c_{Cu} M_B (T' - T_B) + c_{Cu} M_T (T' - T_T) + c_W M_W (T' - T_W) = 0$$

$$0.38 \times 200 (T' - 400) + 0.38 \times 500 (T' - 300) + 4.184 \times 4000 (T' - 300) = 0$$

Solving for the final temperature, we get $T' = 300.45 \text{ K}$.

The change in internal energy of the Cu block is:

$$\Delta U_B = c_{Cu} M_B (T' - T_B) = 0.38 \times 200 \times (T' - 400) = 0.38 \times 200 \times (300.45 - 400) = -7.57 \times 10^3 \text{ J}.$$

The change in internal energy of the water is:

$$\Delta U_W = c_W M_W (T' - T_W) = 4.184 \times 4000 \times (T' - 300) = 4.184 \times 4000 \times (300.447 - 300) = +7.48 \times 10^3 \text{ J}.$$

7. Express the work done by 1 mole of gas, which has the equation of state

$$PV_m = RT + AT - BP$$

when it expands in a reversible isothermal process from volume V_1 to volume V_2 . A and B are characteristic constants of the gas, and V_m is the molar volume.

The reversible work is written as $W = - \int_{V_1}^{V_2} dV P(V, T)$. Therefore, we must first transform the equation in the problem statement into the form $P = P(V, T)$.

$$PV_m = \frac{PV}{N} = RT + AT - BP$$

$$P \left(\frac{V}{N} - AT + B \right) = RT$$

Therefore,

$$P(V, T) = \frac{NRT}{V - (AT - B)N}$$

Now the work can be computed by integration at constant T :

$$W = - \int_{V_1}^{V_2} dV P(V, T) = - \int_{V_1}^{V_2} dV \frac{NRT}{V - (AT - B)N} = - NRT \ln \left(\frac{V_2 - (AT - B)N}{V_1 - (AT - B)N} \right)$$

8. Compute the maximum work that can be obtained from:

- a) an isothermal expansion
- b) an adiabatic expansion

from 2.0 mols of nitrogen, initially at 25°C, from 10 liters up to 20 liters. Assume $c_V = 2.5 R$ and that the gas is ideal. Represent the two transformations in a P-V plane.

First note that this is the c_V molar heat capacity (or heat capacity per unit mol).

The maximum work is the reversible work.

a) Isothermal expansion

For the isothermal process:

$$W^{isoth} = - \int_i^f P(V, T) dV = - \int_{V_i}^{V_f} \frac{NRT}{V} dV = -NRT \ln \frac{V_f}{V_i} = -2 \times 8.314 \times 298.15 \times \ln 2 = -3.44 \times 10^3 \text{ J}$$

b) Adiabatic expansion

For the adiabatic process, a quick way is as follows:

First, recall that for an ideal gas, $dU = C_V dT$. Therefore, for the adiabatic reversible work, $C_V dT = -PdV$, and

$$W^{ad} = - \int_i^f P dV = \int_i^f C_V dT = C_V \int_i^f dT = C_V (T_f - T_i)$$

where $C_V = c_V N$, and where we have used the fact that for an ideal gas C_V is independent of the temperature (is constant). Note that W^{ad} is negative, as the final temperature is colder than the initial temperature.

Now we need to compute T_f , from the available data. Let us in fact, get T_f/T_i .

Recalling from the notes that in an adiabatic process for an ideal gas,

$$\left(\frac{T_f}{T_i} \right)^{\frac{1}{\gamma-1}} = \frac{V_i}{V_f}$$

Therefore,

$$W^{ad} = C_V (T_f - T_i) = C_V T_i \left(\frac{T_f}{T_i} - 1 \right) = C_V T_i \left(\left(\frac{V_i}{V_f} \right)^{\gamma-1} - 1 \right)$$

Now, from C_V , we need to compute the heat capacity ratio, $\gamma = C_P/C_V$. Recalling Meyer's relationship for an ideal gas (see course's slides), $C_P = C_V + NR$, we now introduce $C_V = c_V N = \frac{5}{2} NR$ (diatomic gas at low temperature), to obtain

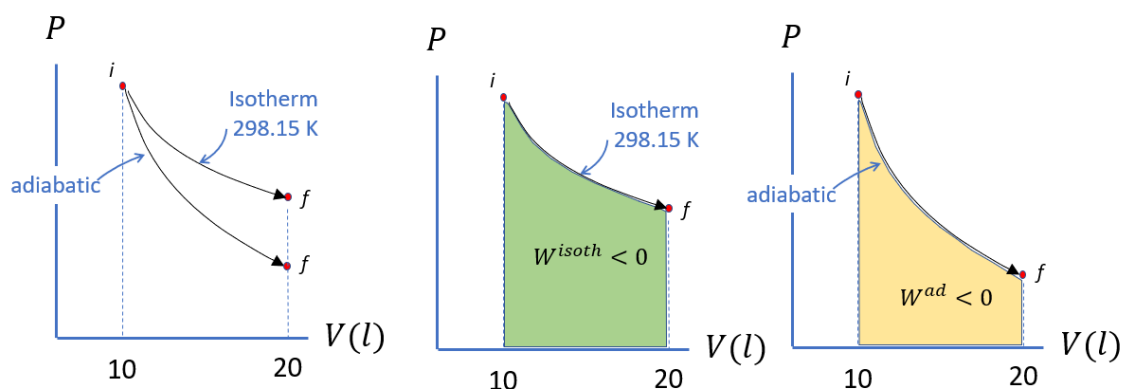
$$C_P = \frac{5}{2} NR + NR = \frac{7}{2} NR, \quad \text{and} \quad \gamma = \frac{C_P}{C_V} = \frac{7}{5}$$

We now have all the inputs to compute the adiabatic work of expansion:

$$W^{ad} = c_V N T_i \left(\left(\frac{V_i}{V_f} \right)^{\gamma-1} - 1 \right) = 2.5 \times 2 \times 8.314 \times 298.15 \times \left(\left(\frac{1}{2} \right)^{\frac{7}{5}-1} - 1 \right)$$

$$= -3.00 \times 10^3 \text{ J}$$

We can represent the two transformations in a P-V plane like this:



9. A 583 m^3 piece of ice at atmospheric pressure and 0°C is heated and becomes water at 4°C . Compute the increase in internal energy. Ice density = 0.917 g cm^{-3} ; water density (l) = 1.00 g cm^{-3} . $c_p(\text{H}_2\text{O}, \text{l}) = 4.180 \text{ J g}^{-1} \text{ K}^{-1}$. Ice's enthalpy of fusion = 80.0 cal g^{-1} .

The internal energy change ΔU should be determined by adding the heat and work contributions:

$$\Delta U = Q + W$$

Let us conceive a two-step process that takes us from the initial state to the final state, which considers (i) the melting at the melting temperature (equal to the initial temperature, 0°C), then (ii) the heating of the water from the melting temperature to the final temperature (4°C). In the process, heat Q is supplied to melt the ice, and then to heat the water. In addition, work W is done by the system.

The process takes place at constant pressure. Therefore, the heat exchanged is equal to the enthalpy change (see notes in class):

$$Q = Q_P = \Delta H|_P$$

The enthalpy change is the sum of the enthalpy changes for the two process stages:

$$\Delta H|_P = M \Delta H_{melt} + M \int_{T_i}^{T_f} dT c_{P,l} = M \Delta H_{melt} + M c_{P,l} (T_f - T_i)$$

where subscript l, refers to liquid water, and we've used the fact that $c_{P,l}$ is considered constant. From the problem statement, we have:

$$\Delta H_{melt} = 80.0 \frac{\text{cal}}{\text{g}} = 334.7 \frac{\text{J}}{\text{g}}$$

$$c_{P,l} = 4.180 \frac{\text{J}}{\text{gK}}$$

where we have transformed the units of the first item by considering that $1 \text{ cal} = 4.184 \text{ J}$.

Note we are keeping grams for mass units, as all the inputs are using grams for mass units, and these will go away in the computation of heat.

Next, we compute the mass from the density of ice and initial volume:

$$M = 583 \text{ m}^3 \times 0.917 \frac{\text{g}}{\text{cm}^3} \times \left(\frac{100 \text{ cm}}{\text{m}}\right)^3 = 5.346 \times 10^8 \text{ g}$$

Now we can finally compute the heat, as:

$$Q_P = \Delta H|_P = M \Delta H_{\text{melt}} + M c_{P,l} (T_f - T_i) = 1.879 \times 10^{11} \text{ J}$$

It is interesting to note that the contribution from the melting is 20 times bigger than the contribution from the heating.

Now we need to compute the work. To do so, we realize that the external pressure P_{ext} is constant, equal to $1 \text{ atm} = 101325 \text{ Pa}$. The work is simply:

$$\begin{aligned} W &= \int_{V_i}^{V_f} -P_{\text{ext}} dV = P_{\text{ext}} (V_i - V_f) = P_{\text{ext}} M \left(\frac{1}{\rho_i} - \frac{1}{\rho_f} \right) = P_{\text{ext}} M \left(\frac{1}{\rho_{\text{ice}}} - \frac{1}{\rho_l} \right) \\ &= 101325 \text{ Pa} \times 5.346 \times 10^5 \text{ kg} \times \left(\frac{1}{917} - \frac{1}{1000} \right) \frac{\text{m}^3}{\text{kg}} \\ &= 4.903 \times 10^6 \text{ J} \end{aligned}$$

The work is positive as the system contracts in the melting process (as the volume is reduced because the density of ice is lower than that of water). Nonetheless this quantity is much smaller than Q by 5 orders of magnitude. In the end we have that the change in internal energy has a positive contribution from the heat absorbed (where 95% is used for melting) and a positive contribution from the work of contraction, which is negligible in comparison, such that,

$$\Delta U = Q + W = 1.879 \times 10^{11} \text{ J} + 4.903 \times 10^6 \text{ J} \approx \Delta H|_P = \mathbf{1.879 \times 10^{11} \text{ J}}$$
