# Thermodynamics. Problems. Sheet 3.

Solutions of the problems.

1. A certain amount of ideal gas ($c_{p,molar}$= 7R/2) at 20°C and 1 atm, has a volume of 70 m³ and is heated at constant pressure to 25°C by heat transfer from a thermal reservoir at 40°C.

   a) What is the heat transferred to the gas?
   b) Is the process irreversible?
   c) What is the change in entropy of the thermal reservoir?
   d) What is the change in entropy of the gas?

<u>Preliminaries:</u>

Initially, we may assume that the reservoir T 40°C and the gas at 20°C are separated by an adiabatic wall. Suddenly, we turn it into a diathermic wall. Heat transfer will initiate until the wall is made adiabatic again. When a new equilibrium (final) state is reached in the gas, its temperature equals 25°C. The **pressure** remains constant through the entire process, at 1 atm. This means, therefore, that the system is in contact with a pressure source (ambient surroundings) through an adiabatic piston which moves throughout the process as needed, to maintain the pressure of the gas system constant.
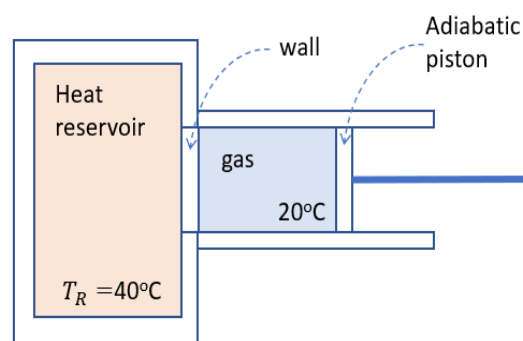
The molar heat capacity suggests that the gas is diatomic at low temperature. We thus identify the **system** as the ideal gas. Now we need to identify all the necessary variables at the **initial (i) and the final (f) states** for the gas. What we know is:

$V_i = 70$ m³

$T_i = 273.15 + 20 = 293.15$ K

$T_f = 273.15 + 25 = 298.15$ K

$P_i = P_f = 1$ atm $= 101325$ Pa

From the i-state info, we compute the number of moles (by the ideal gas eq. of state):

$$N = \frac{P_i V_i}{RT_i} = \frac{101325 \text{ Pa} * 70 \text{ m}^3}{8.314 \text{ J(mol K)}^{-1} * 293.15 \text{ K}} = 2.910 \cdot 10^3 \text{ mol}$$

The final volume V_f is not needed in the problem, as will be seen later; but it could easily be computed from the initial volume and the initial and final temperatures, and Charles' law (the ideal gas law when P and N remain constant:

$$V_f = V_i * (T_f/T_i)$$

a) Since the gas temperature has been raised in the process by heat transfer, we can compute the heat transfer assuming it was done reversibly (even if it had not been done so in reality). Therefore, to compute the heat transferred, we can write:

$$dQ|_P = dH|_P = C_P dT = c_{Pm} N dT$$

$$Q = \int dQ|_P = \int_{T_i}^{T_f} c_{Pm} N dT = \int_{T_i}^{T_f} \frac{7}{2} RN dT = \frac{7}{2} RN(T_f - T_i) =$$

$$= \frac{7}{2} 8.314 * 2.910 \cdot 10^3 * 5 = \mathbf{4.234 * 10^5} \text{ Joules}$$

where we have used the gas temperature difference of 5 K.

b) It is an **irreversible** process due to the finite temperature difference existing between the reservoir and the system while they are in contact (during the heat transfer process). The process is spontaneous, thus irreversible.

c) To compute the entropy change of the thermal reservoir, we conceive a reversible process that takes the system in question (the reservoir, in this case) from the initial state to the final state (both being equilibrium states). In this case the process must be a heat transfer at constant temperature, equal to the reservoir's temperature, T_R. We imagine that we separate it from the ideal gas subsystem by an **adiabatic rigid wall**, and then connect it to a system that can remove heat reversibly **at the constant temperature of the reservoir**, for example, a **Carnot engine**, such that, in one or more cycles, the engine **reversibly** removes the amount of heat computed in a). (We would be assuming that the cold sink for the engine is the ambient, and therefore, that the ambient is colder than the heat reservoir; however, the details of this part are of no consequence in the computation.) By definition of how a reservoir works in such a process, the reversible heat exchange will take place at constant temperature (as it is a heat reservoir). The entropy change in the thermal reservoir is therefore easily computed as:

$$\Delta S_r \equiv \int \frac{dQ^{rev}}{T} = \int \frac{dQ^{rev}}{T_R} = \frac{1}{T_R} \int dQ^{rev} = \frac{-Q}{T_R} = \frac{-4.23 * 10^5 \text{ J}}{313.15 \text{ K}}$$
$$= -\mathbf{1.352 * 10^3} \frac{\mathbf{J}}{\mathbf{K}}$$

Note that the heat is negative, as it leaves the reservoir, and is equal to minus the heat gained by the gas system in the real process Q, computed in a).

d) To compute the change of entropy in the gas subsystem, we conceive a reversible process by which the gas can evolve from its initial to its final state. Instead of obtaining heat (irreversibly) from the heat reservoir, as stated in the problem, the gas obtains it reversibly (at constant pressure), for example from the ambient by means of a Carnot refrigerator. Because the temperature is changing through the process, we imagine that the Carnot cycles are taking place with a progressively changing temperature. This does not contradict the Carnot cycle (which assumes isothermal stages) if many differential Carnot cycles are used sequentially, each designed to work between a cold source temperature and the system temperature. In addition, we maintain the constant pressure condition during the conceived reversible process by a frictionless adiabatic piston connected to a mechanical implement which, through the process, raises a weight in the gravitational field. (We say 'raises' instead of 'lowers', as the system expands and, therefore, does work on the surroundings.) The details of this has no impact on the entropy, as reversible work interactions have no effect on the system entropy. Summing up, the change of entropy for the gas is:

$$\Delta S_{gas} = \int_{T_i}^{T_f} \frac{dQ|_P^{rev}}{T} = \int_{T_i}^{T_f} \frac{c_{Pm}NdT}{T} = c_{Pm}N \int_{T_i}^{T_f} \frac{dT}{T} = c_{Pm}N \ln\frac{T_f}{T_i}$$

$$= \frac{7}{2} 8.314 * 2.91 \cdot 10^3 \ln\frac{298.15}{293.15} = \mathbf{1.432 * 10^3} \frac{\mathbf{J}}{\mathbf{K}}$$

Note that we could have arrived at the same result with a different path, for example, an isochoric heating followed by an isothermal expansion (see class notes).

Additional comments

1) It is interesting to ask: What is the net entropy change caused by this process on the 'universe' defined as the sum of the reservoir plus the gas system, plus the surroundings with which the gas interacts?

$$\Delta S = \Delta S_r + \Delta S_{gas} + \Delta S_{surround}$$

We already computed the first two terms, and they add to a net positive value

$$\Delta S_r + \Delta S_{gas} = 80.1 \text{ J/K}$$

We need to further enquire about the entropy change $\Delta S_{surround}$, due to the work interaction between the system and the surroundings. We need to enquire about the nature of the interaction of the gas with the surroundings. It is a non-negligible work interaction ($W=0.29(-Q)$), carried out at constant pressure. Since, the process happens at constant pressure by definition, the work can be used to raise a weight in the gravitational field. In this case, the effect on the entropy of the surroundings is zero, and

$$\Delta S = \Delta S_r + \Delta S_{gas} = 80.1 \frac{\text{J}}{\text{K}} > 0$$

as expected for an irreversible process.

2) It is also interesting to ask whether the entropy changes in the ambient **in the fictitious processes**, namely the two processes combined, by which heat is first removed reversibly from the reservoir by means of a heat engine, and then the same amount of heat is injected reversibly into the gas by means of a heat pump (while it expands reversibly, doing reversible work on its surroundings)? Since only reversible heat transfer and work are considered in the fictitious processes, the global change in entropy must be 0. Therefore, the ambient must have experienced an overall entropy change of -80.1 J/K.

$$\Delta S_{surround} = \Delta S - (\Delta S_r + \Delta S_{gas}) = 0 - 80.1\frac{\text{J}}{\text{K}} = -80.1 \text{ J/K}$$

2. A rigid container with a volume of 50 dm^3 contains an ideal gas ($c_{v,molar} = 5R/2$) at 500 K and 1 atm.

   a) Compute the change in entropy of the gas if 2870 cal are transferred to it as heat.
   b) If the vessel has a stirrer that rotates such that the shaft's work delivered to the gas equals 12.0 kJ, compute the entropy change of the gas if the process is adiabatic.
   c) Compute the total entropy in stage b. Is the process irreversible?

Preliminaries:

The system is an ideal gas in a rigid container with diathermal walls connecting it thermally to a heat source of some kind.

We also need to identify the initial and the final states. We know $V_1 = V_2 = 50$ dm^3 = 0.05 m^3, $T_1 = 500$ K, $P_1 = 1$ atm = 103125 Pa. As the gas heats up at constant volume, its pressure will increase. We need to find N, P_2 and T_2. Once we know one, we can easily compute the other, by applying the ideal gas law: $PV = NRT$.

$$N = \frac{P_1 V_1}{RT_1} = \frac{101325 \text{ Pa} * 0.05 \text{ m}^3}{8.314 \text{ J(mol K)} * 500\text{K}} = 1.218 \text{ mol}$$

a) We will need the final temperature to do the integral of the entropy. To compute T_2, we use the ideal gas law: $U = c_{vm}NT$, and apply the First Law to the process: $\Delta U = Q + W = Q$ (as W is 0). Since c_{vm} and N are constant.

$$Q = \Delta U|_V = \int_{T_1}^{T_2} c_{vm}NdT = c_{vm}N(T_2 - T_1)$$

Therefore, we can solve for T_2, as Q is known

$$T_2 = T_1 + \frac{Q}{c_{vm}N} = \cdots = 974 \text{ K}$$

In doing this calculation, one must remember to use consistent units. Particularly, since we use SI units, one must convert the 2870 cal to joules (2870*4.186=12014 J).

As entropy is a state variable, to compute the entropy change we can conceive a process by which 2870 cal are transferred <u>reversibly</u> to the gas from some heat source. For the heat transfer to be reversible, the temperature of the heat source is lowered to the ideal gas temperature (which varies through the process), and then it is elevated infinitesimally (so very slightly) so that the process can be considered reversible. Each infinitesimal of heat transferred in this manner satisfies:

$$dQ|_V = C_V dT = c_{Vm}NdT$$

Therefore, we can integrate the expression for the entropy as follows:

$$\Delta S_{gas} = \int_{T_1}^{T_2} \frac{dQ^{rev}}{T} = \int_{T_1}^{T_2} \frac{c_{Vm}NdT}{T} = c_{Vm}N \int_{T_1}^{T_2} \frac{dT}{T} = c_{Vm}N \ln\frac{T_2}{T_1}$$
$$= \frac{5}{2}8.314 * 1.218 \ln\frac{974}{500} = \mathbf{16.9}\frac{\mathbf{J}}{\mathbf{K}}$$

b) This is akin to Joule's paddle wheel experiment. The shaft work is adiabatic irreversible work. Again, we need to compute the final temperature, and again we

make use of the first law applied to the process, where now $Q = 0$ (adiabatic process).

$$W = \Delta U = c_{vm} N \Delta T = c_{vm} N (T_2 - T_1)$$

Therefore, we can again solve for T_2, as W is known

$$T_2 = T_1 + \frac{W}{c_{vm}N} = \cdots = 974 \text{ K}$$

To compute ΔS we again imagine a <u>reversible</u> process taking the system from its initial state to its final state. We consider reversible heating from some heat source at constant volume (isochoric). For this process,

$$dQ|_V = C_V dT = c_{Vm} N dT$$

and we can integrate the expression for the entropy, similarly as in section a), as follows:

$$\Delta S_{gas} = \int_{T_1}^{T_2} \frac{dQ^{rev}}{T} = \int_{T_1}^{T_2} \frac{c_{Vm} N dT}{T} = c_{Vm} N \int_{T_1}^{T_2} \frac{dT}{T} = c_{Vm} N \ln \frac{T_2}{T_1}$$

$$= \frac{5}{2} 8.314 * 1.218 \ln \frac{974}{500} = \mathbf{16.9 \frac{J}{K}}$$

The value coincides because the final temperature and energy transferred are the same in both problems.

c) In b) the entropy change outside is 0 because no heat is transferred in the process of doing shaft work. The work can be delivered in a conservative manner; such as by lowering a weight or releasing a spring, and such a process does not change the entropy of the ambient. Therefore, the total entropy change is:

$$\Delta S = \Delta S_{surroundings} + \Delta S_{gas} = (0 + 16.9) \frac{J}{K} = \mathbf{16.9 \frac{J}{K}} > 0$$

This is positive, as expected for an irreversible process.

3. Very pure liquid water can be subcooled at atmospheric pressure to temperatures well below 0°C. One kilogram of liquid water chilled to -6°C partially freezes in an adiabatic process at atmospheric pressure.

a) What fraction of the system freezes?
b) What is its final temperature?
c) What is the ΔS_{total} for the process?
d) Is the process reversible or irreversible?

$\Delta H_{melting}$ of water at 0°C = 333.4 J g^{-1}.
c_p of subcooled liquid water = 4.226 J g^{-1} °C^{-1}.

Preliminaries: In this problem, the system composed of the liquid water and the ice can be considered closed and surrounded by adiabatic walls. The water has been supercooled to a temperature (-6°C) below its equilibrium (freezing) temperature (0°C). This is not, in fact, an equilibrium state. During this process no heat is either added or removed from it; therefore, the process is **adiabatic**. Therefore, the system uses its own energy to evolve to an equilibrium state. It does so by freezing part of its water (a fraction x of its initial mass M), and using the "released" latent heat of solidification to raise the system's temperature. This continues until the equilibrium temperature is reached. Because the process occurs at constant pressure, there is work interaction with the surroundings; and therefore, the system is not isolated. This means we will be using enthalpy to analyze the energy balance in a) below. Nevertheless, the work interaction is very small compared to the latent heat released (and will not have to be analyzed, anyway).

1 atm

-6 → 0°C
water
$M(1 - x)$

ice Mx
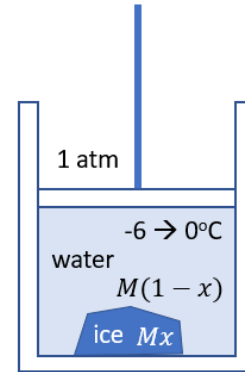
b) We can first answer this question: The **equilibrium final temperature** T_f is the freezing temperature of water, namely 0 °C. It is the equilibrium temperature of water and ice at 1 atm. (Note, it would change at another pressure; a topic reviewed later on in the course)

a) We compute the fraction of the water that freezes, by use of the First Law (energy must be conserved in the process). It is an adiabatic process ($Q = 0$) taking place at constant pressure. Constant pressure means that the work interaction with the surroundings, associated with the displacement of the piston, (W) is non-zero. We conceive a path connecting the initial and the final equilibrium states (the first being a metastable equilibrium state), consisting of 2 stages:

Stage A: All of the liquid water in the system is reversibly heated up (warmed up) from -6°C to 0°C (T_f). We imagine that heat is (temporarily) borrowed from a hypothetical external heat source.

Stage B: A fraction x of the mass of the water at T_f (0°C) freezes at constant temperature, becoming ice. In doing so, it releases latent heat in the same exact amount as was taken up in stage 1, and so this latent heat is returned to the hypothetical heat source.

The system is 'mechanically reversible' as the work in this problem can simply be stored as mechanical energy, e.g., by raising a weight in the gravitational field or by compressing a spring (see also Levine #2.9).

To compute x, we apply the First Law; however, instead of using U, in a constant-pressure adiabatic process it is more convenient to use the enthalpy, H, to describe the system evolution at constant pressure. The reason for this is that through an adiabatic (reversible) process $\Delta H|_P^{ad} = 0$. (To see this, let us recall that $H = U + PV$. Therefore, $dH = dQ + VdP$ for reversible work. At constant pressure $VdP = 0$, while in an adiabatic process $dQ^{ad} = 0$. Therefore, $dH|_P^{ad} = 0$. Therefore, $\Delta H|_P^{ad} = 0$.) This means that

$$\Delta H|_P^{ad} = \Delta H_1 + \Delta H_2 = 0$$

where the subscripts refer to process stages 1 and 2.

Let us now compute each addend separately, so we can plug them in again here to obtain an equation for x:

ΔH_A: **Enthalpy change for stage A.-** We are imagining that some heat source is supplying heat to the system to raise its temperature from -6ºC to 0ºC, without any phase change. The change is enthalpy is:

$$\Delta H_A = Mc_p\left(T_f - T_i\right) =$$

$$1000\text{g} \times 4.226\ \text{Jg}^{-1}\text{K}^{-1} \times 6\text{K} = 25356\ \text{J}$$

ΔH_B: **Enthalpy change for stage B.-** We now consider the freezing stage at constant pressure and temperature (1 atm, 0ºC) of a mass of water xM. In doing so, the enthalpy of this water is reduced by the product of the frozen mass and the enthalpy of solidification per unit mass Δh_{soli}, which is minus the enthalpy of melting per unit mass $\Delta h_{melting}$:

$$\Delta H_B = xM\Delta h_{soli} = xM\left(-\Delta h_{melting}\right) = -x * 1000\text{g} * 333.4\ \text{Jg}^{-1}$$

We show the computations for the benefit of the reader, but it is better not to perform them at this stage.

Now we plug each enthalpy change into $\Delta H|_P^{ad} = \Delta H_1 + \Delta H_2 = 0$ (justified earlier). We get a linear equation for x, which can be solved trivially:

$$Mc_p\left(T_f - T_i\right) - xM\Delta H_{melting} = 0$$

$$x = \frac{c_p\left(T_f - T_i\right)}{\Delta h_{melting}} = \frac{4.226\ \text{Jg}^{-1}\text{K}^{-1} \times 6\text{K}}{333.4\ \text{Jg}^{-1}} = \mathbf{0.07605 = 7.6\%}$$

Note that, as expected, this result is independent of M (as this variable cancels out).

c) To compute the **entropy change,** we compute the entropy change for the two stages above. There is no other source of entropy, since the system is not exchanging heat with its surroundings, and the mechanical work (due to changes in the system volume) is not contributing to the entropy balance. The entropy changes for stages 1 and 2 are as follows:

$$\Delta S_A = \int_{T_i}^{T_f} \frac{dQ|_P}{T} = \int_{T_i}^{T_f} \frac{M c_P dT}{T} = M c_P \int_{T_i}^{T_f} \frac{dT}{T} = M c_P \ln \left(\frac{T_f}{T_i} \right)$$

$$= 1000 * 4.226 * \ln \left(\frac{273.15}{273.15 - 6} \right) = 93.863 \frac{J}{K}$$

$$\Delta S_B = \int \frac{dQ|_P}{T} = \frac{1}{T_f} \int dQ|_P = \frac{\Delta H_2}{T_f} = \frac{x M \Delta H_{soli}}{T_f} = \frac{0.07605 * 1000 * (-333.4)}{273.15}$$

$$= -92.828 \frac{J}{K}$$

The total entropy change is:

$$\Delta S = \Delta S_A + \Delta S_B = (93.863 - 92.828) \frac{J}{K} = \mathbf{1.03} \frac{J}{K} > 0$$

d) It is an **irreversible** process, because it is spontaneous.

Additional comment:

Note that the real process does not happen at well-defined equilibrium temperature. It starts at -6°C in a state of metastable equilibrium (non-equilibrium but uniform temperature and pressure), and, as ice forms, latent heat is released, thus raising the system temperature, which may not stay uniform in the system during the process. The final equilibrium state is stable at 0°C, the melting temperature of ice at 1 atm. The system is stable because a slight spontaneous upwards excursion of the temperature of the system would cause ice to melt the system equilibrates to a final equilibrium temperature of 0°C.

Note also that although we made provisions for maintaining the pressure constant, the work interaction is small, as the volume change is relatively small.

4. Compute the entropy change that occurs when a 50-gram block of iron at a temperature of 90°C (c_p= 0.449 J/g K) is placed in an insulated container containing 100 g of water (c_p= 4180 J kg^{-1} K^{-1}) at 25°C. Is the process irreversible? Why? Consider the heat capacities to be constant within the working temperature range.

a) Yes, it is **irreversible**, because it is a fast process without intermediate equilibrium states. All reversible processes are quasi-static. All non-quasi-static processes, like this one, are irreversible.

b) **Entropy computation:** We design a reversible process taking the system from the initial to the final state. The system is defined as the iron block and the water. The system is heat insulated; this means that the process is adiabatic, as no heat interactions happen with the surroundings. In the reversible process we conceive, the iron block is first cooled to the final temperature T_2, and the water bath is heated to that same temperature T_2. Both temperatures are the same, which can be computed by applying the First Law to the process. For the system composed of the iron block (subscript b) and the water bath (subscript w):

$$\Delta U = \Delta U_b + \Delta U_w = Q + W$$

Since, from the information give, we can assume that the process is carried out at constant pressure, we have that for this process

$$\Delta H|_P = Q = 0$$

since no heat is exchanged with the surroundings. Now, we can decompose H as:

$$H = H_b + H_w$$

And the First Law, in this problem, therefore states that

$$\Delta H = \Delta H_b + \Delta H_w = 0$$

We can express ΔH_b and ΔH_w as the products of heat capacities and the temperature differences:

$$\Delta U_b + \Delta U_w = c_{pb} M_b (T_2 - T_{b1}) + c_{pw} M_w (T_2 - T_{w1}) = 0$$

(Note that the first addend is negative while the second addend is positive.) From this, we can solve for the unknown final temperature T_2.

$$T_2 = \frac{c_{pb} M_b T_{b1} + c_{pw} M_w T_{w1}}{c_{pb} M_b + c_{pw} M_w} = 301.45 \text{ K}$$

Since the M's are given in grams, it may be convenient to have the c_p's in J/g K, which for water is c_{pw}= 4.18 J g^{-1} K^{-1} (given in SI units in the problem statement).

To compute the entropy change we simply integrate for the reversible process designed above:

$$\Delta S = \Delta S_b + \Delta S_w = \int_{T_{1b}}^{T_2} \frac{dQ^{rev,b}}{T} + \int_{T_{1w}}^{T_2} \frac{dQ^{rev,w}}{T} = \int_{T_{1b}}^{T_2} \frac{c_{pb}M_b dT}{T} + \int_{T_{1w}}^{T_2} \frac{c_{pw}M_w dT}{T}$$

$$= c_{pb}M_b \int_{T_{1b}}^{T_2} \frac{dT}{T} + c_{pw}M_w \int_{T_{1w}}^{T_2} \frac{dT}{T} = c_{pb}M_b \ln\frac{T_2}{T_{1b}} + c_{pw}M_w \ln\frac{T_2}{T_{1w}}$$

$$= 0.449 * 50 * \ln\left(\frac{301.45}{273.15 + 90}\right) + 4.180 * 100 * \ln\left(\frac{301.45}{273.15 + 25}\right)$$

$$= -4.1802 + 4.6201 = \mathbf{0.440}\,\frac{\mathbf{J}}{\mathbf{K}}$$

The value is positive as expected for a spontaneous process. (Recall that the heat interaction at constant pressure does not contribute to the entropy change; see problem 3).

Note that the argument in the second logarithm is very close to unity, and therefore, the ln will be close to zero. This means that small errors in the temperatures will lead to large errors in the result. If this term was negligible in the overall computation, we could forget about this matter. However, since this is not the case, the end result is very sensitive to errors in the temperatures entered in the argument of the second logarithm. The same problem does not exist with the first logarithm. For example, if we had taken 301K and 363 K, the first entropy contribution would be -4.20 instead of -4.18 J/K. This would have impacted the final result at the 5% level of 0.42 J/K (10% if we had used 302 instead of 301). However, the second entropy contribution with 301 K and 298 K would give us 4.19 J/K, very far from the correct value of 4.620 J/K, and thus lead to a huge error in the final calculation.

5. Compute the change in internal energy, enthalpy and entropy for the expansion of 10 mol of oxygen from 200 to 2000 liters at 25°C.

The expansion is done isothermally. Therefore, the system does isothermal work.

Since we are not given additional information, we are allowed to presuppose that oxygen behaves as an ideal gas. (In reality, we would actually have to evaluate how closely oxygen behaves as an ideal gas at the temperature and pressures involved. In reality, the ideal gas equation is a good approximation, as the critical temperature and pressure are 'far' from the conditions of the problem: $T_C = 155$ K, $P_C = 50$ bar. The highest pressure in the problem is approximately, $P = \frac{NRT}{V} = \frac{10*8.314*298}{0.2} = 1.2$ bar.)

a) The internal energy depends only on the temperature. Therefore, in an isothermal expansion, the **change in internal energy** is zero:

$$\Delta U = 0 \text{ (isothermal, ideal gas)}$$

b) The **change in enthalpy** is also zero:

$$\Delta H \equiv \Delta(U + PV) = \Delta(PV) = \Delta(NRT) = NR\Delta T = \mathbf{0}$$

where the ideal gas law $PV = NRT$ was invoked.

c) The **entropy change** can be computed designing a reversible process, in this case an isothermal expansion, that takes us from the initial state to the final state. In this case,

$$\Delta S = \int \frac{dQ^{rev}}{T} = \frac{1}{T}\int dQ^{rev} = \frac{Q^{rev}}{T}$$

To get Q^{rev}, we apply the First Law to the process:

$$Q^{rev} = \Delta U - W^{rev} = 0 - W^{rev} = -W^{rev} = -\int_{V_1}^{V_2} -PdV = \int_{V_1}^{V_2} \frac{NRTdV}{V}$$

$$= NRT \ln\frac{V_2}{V_1} = 10 * 8.314 * (273.15 + 25) * \ln\left(\frac{2000}{200}\right) = 57.1 \text{ kJ}$$

Note that the work is negative, as expected for an expansion.

We can now easily compute the entropy change as

$$\Delta S = \frac{57.1 * 10^3 \text{ J}}{298.15 \text{ K}} = \mathbf{191\frac{J}{K}}$$

The entropy change is positive, as expected for any isothermal expansion, in which the system absorbs heat.

6. A plant operates with a source at 300°C and a sink at 25°C. If the thermal efficiency is equal to 60% of that of a Carnot engine for the same temperatures,

a) What is the thermal efficiency of the plant?

b) What increase must be given to the source temperature so that the thermal efficiency of the plant increases to 40%? Again, η is equal to 60% of the value corresponding to the Carnot engine.

a) The efficiency η, defined as $|W|/|Q_H|$, is 0.6 times the Carnot efficiency η_C

$$\eta_C = 1 - \frac{T_C}{T_H}$$

T_H being the source temperature, namely T_H=273.15+300=573.15 K, and T_C being the sink temperature, namely T_C=273.15+25=298.15 K.

Therefore, the thermal efficiency of the plant is equal to:

$$\eta = 0.6\,\eta_C = 0.6 * \left(1 - \frac{T_C}{T_H}\right) = 0.6 * \left(1 - \frac{298.15}{573.15}\right) = 0.6 * 0.480 = \mathbf{0.288}$$
$$= \mathbf{28.8\%}$$

b) Now, to increase the efficiency of the plant to 40% (not by 40%!) we will have to raise the heat source temperature to a new T_H, such that

$$0.6 * \left(1 - \frac{T_C}{T_{H,new}}\right) = 0.4$$

where T_C=298.15 K (same as before). Therefore,

$$T_{H,new} = \frac{T_C}{1 - \frac{0.4}{0.6}} = \frac{T_C}{1 - \frac{2}{3}} = 3T_C = 3 * 298.15 = \mathbf{894\ K}$$

7. A heat engine works between a hot source at 900 K and a cold source at 300 K following a reversible Carnot cycle. The work produced is used in operating a crane. If 10% of the work of the heat engine is lost in the form of heat due to friction of the pulleys and the total amount of heat given off by the heat engine-pulleys assembly is 72 kJ, compute the heat absorbed from the hot source, the work done by the engine, and the heat transferred to the coolant (cold source).

Overall, we basically need to balance the energy exchanges everywhere while fulfilling the conditions given in the problem statement.

The heat absorbed from the hot source $|Q_H|$ is related to the work output W through the efficiency η, which for the reversible heat engine can be computed as:

$$\eta = \frac{|W|}{|Q_H|} = 1 - \frac{T_C}{T_H} = 1 - \frac{300}{900} = 2/3$$

Therefore,

$$\frac{|W|}{|Q_H|} = 2/3$$

We also have that the heat given off is the heat going to the cold source plus 10% of the work:

$$Q_{off} = |Q_C| + 0.1|W| = 72000 \text{ J}$$

Finally, because the heat engine works in cycles, the net internal energy change in a cycle is zero, and we must have that:

$$|Q_H| = |Q_C| + |W|$$

We have three equations and three unknowns: $|Q_H|$, $|Q_C|$, $|W|$. One way to solve this is to eliminate $|Q_C|$ from the last two equations,

$$|Q_H| - |W| + 0.1|W| = |Q_H| - 0.9|W| = 72000 \text{ J}$$

And then substitute $2|Q_H|/3$ for $|W|$ obtained from the first expression, to obtain:
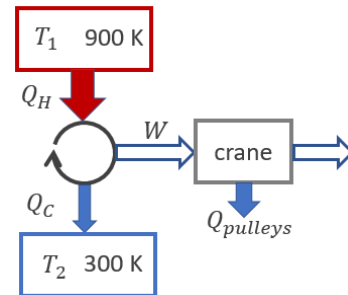
$$|Q_H|(1 - 0.9\frac{2}{3}) = 72000 \text{ J}$$

Wherefrom, we can easily get the value of $|Q_H|$, then retrace our steps to find the other values:

The heat absorbed from the hot source: $|Q_H| = 180$ kJ

The work done by the engine: $|W| = 120$ kJ

The heat transferred to the coolant: $|Q_C| = 60$ kJ

8. The work obtained from a heat engine operating between 1200°C and 25°C, following a reversible Carnot cycle, is used to operate a Carnot refrigerating engine operating between 0°C and 25°C. Compute the relationship between the heat absorbed by the heat engine and the heat extracted ~~from~~ by the refrigerating engine if it is assumed that both work reversibly.

Let us define T_1, T_2 and T_3 as the indicated temperatures, in this order (already in Kelvin): T_1=1473.15 K, T_2=298.15, T_3=273.15 K. We can represent the arrangement as in the figure, which also defines the (reversible) heat and work interactions involved:
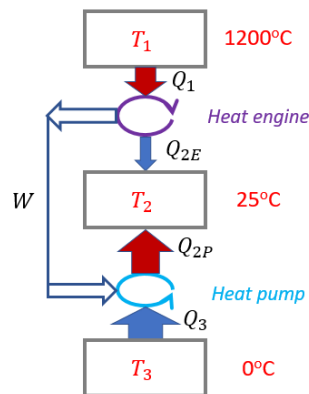
We are asked to compute $\frac{|Q_1|}{|Q_3|}$.

We can compute the **efficiency η** for the Carnot heat engine, and the **coefficient of performance ε** for the Carnot refrigerator as (see class notes):

$$\eta = \frac{|W|}{|Q_1|} = 1 - \frac{T_2}{T_1} = 1 - \frac{298.1}{1473} = 0.800$$

$$\varepsilon = \frac{|Q_3|}{|W|} = \frac{T_3}{T_2 - T_3} = \frac{273.15}{298 - 273} = 10.92$$

What they ask us for is:

$$\frac{|Q_1|}{|Q_3|} = \frac{1}{\eta \varepsilon} = \frac{T_1(T_2 - T_3)}{T_3(T_1 - T_2)} = \frac{1}{0.800 * 10.92} = \mathbf{0.115}$$