

**Problem 5.2 [FOR ASSIGNMENT 3; max 10 points]**

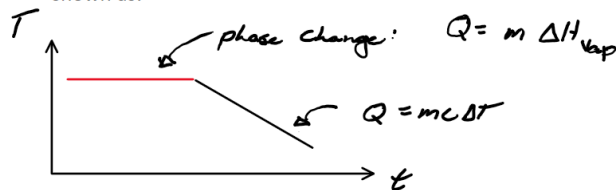
**The entropic cost of condensing.**

A block of copper of mass 2.00 kg ( $c_P = 0.3851 \text{ J/g.K}$ ) and temperature  $0^\circ\text{C}$  is introduced into an insulated container in which there is 1.00 mol  $\text{H}_2\text{O(g)}$  at  $100^\circ\text{C}$  and 1.00 atm. Note that  $c_P = 4.184 \text{ J/g.K}$  for liquid water, and that  $\Delta_{\text{vap}}H = 2260 \text{ J/g}$  for water.

Assuming all the steam is condensed to water, and that the pressure remains constant:

- (a) What will be the final temperature of the system?
- (b) What is the heat transferred from the water to the copper?
- (c) What is the entropy change of the water, the copper, and the total system?

a) We understand the interaction taking place between the cold copper and water gas to involve the full state change from gas to liquid. As such, the typical thermal equilibrium equation will involve a more complex heat transfer, with some going towards the formation of the liquid water as opposed to the temperature. This is shown as:



The heat is first used to convert the gaseous water to a liquid:

$$Q = m \Delta H_{\text{vap}} = \underbrace{1 \times 18}_{\text{g}} \times 2260 \frac{\text{J}}{\text{g}} = 40680 \text{ J}$$

Notice that this does not affect the temperature of the gas, but it does however cool the copper mass by the quantised amount:

$$Q = m c \Delta T \quad \begin{aligned} Q &= 40680 \\ c &= 0.3851 \text{ J/g.K} \\ T_i &= 0^\circ\text{C} = 273 \text{ K} \end{aligned}$$

$$m = 2 \text{ kg} = 2000 \text{ g}$$

$$+ 40680 = 2000 \times 0.3851 \times (T_f - 273)$$

$$T_f = \frac{+ 40680}{2000 \times 0.3851} + 273$$

$$= 329.8 \text{ K}$$

We are now left with 1 mol of liquid water at 373K and a 2kg copper block at 329.8K, thus given no more state changes are present, we can calculate the final temperature.

$$Q = mc\Delta T \quad Q_{\text{water}} = -Q_{\text{copper}}$$

$$\therefore (1 \times 18) \times 4.184 \times (T_f - 373) = -2000 \times 0.3581 \times (T_f - 329.8)$$

$$T_f (75.312 + 716.2) = 236202.76 + 28091.376$$

$$T_f = 333.9\text{K} = 60^\circ\text{C}$$

b)

As the copper mass undergoes no phase change, all the heat transferred went into changing the temperature. As such we understand the total heat change to be the heat required to take the mass from 273K to 333.9K:

$$\begin{aligned} \Delta Q_{\text{copper}} &= mc\Delta T \\ &= 2000 \times 0.3581 \times (333.9 - 273) \\ &= 43616.58\text{J} \end{aligned}$$

c)

For water we understand the substance to experience two separate changes in entropy, the change experienced during phase change, and the change as the temperature is decreased. We can solve for the entropy change as follows:

$$\begin{aligned}
\Delta S_{\text{water}} &= \Delta S_{\text{phase}} + \Delta S_{\text{DT}} \\
&= \frac{\Delta H}{T} + \int_{T_i}^{T_f} \frac{dQ}{T} \\
&= -\frac{40680}{373} + \int_{373}^{333.9} \frac{4.184}{T} dT \times 18 \quad \text{mass} \\
&= -109.1 + 4.184 [\ln(T)]_{373}^{333.9} \times 18 \\
&= -116.94 \text{ J/K}
\end{aligned}$$

For copper, the process is much more simple, only having to consider the change in temperature:

$$\begin{aligned}
\Delta S_{\text{copper}} &= \int_{T_i}^{T_f} \frac{dQ}{T} \\
&= \int_{273}^{333.9} m C_p \frac{1}{T} dT \\
&= 0.3851 [\ln(T)]_{273}^{333.9} \times 2000 \\
&= 155.1 \text{ J/K}
\end{aligned}$$

Then, for the entropy change of the entire system we sum the change of each component:

$$\begin{aligned}
\Delta S_{\text{system}} &= \Delta S_{\text{water}} + \Delta S_{\text{copper}} \\
&= -116.94 + 155.1 \\
&= 38.2 \text{ J/K}
\end{aligned}$$

**Problem 5.5 [FOR ASSIGNMENT 3; max 10 points]**

**Reversible vs. irreversible expansions.**

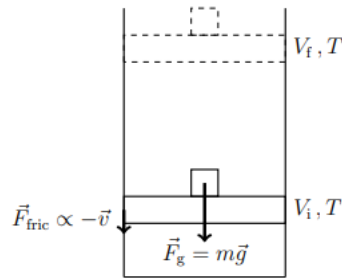


Figure 2: The piston moves inside the cylinder. The friction force acts against the movement of the piston. An external force  $mg$  is applied downward during an irreversible expansion. The final position of the piston is the state of mechanical equilibrium when the force caused by the pressure of the gas equals the external force.

One mol of an ideal gas at  $P_i = 30.0$  bar and  $V_i = 5.0$  L undergoes expansion in three different ways (one reversible and two irreversible). The final temperature of the gas equals its initial temperature in all three cases. Figure 2 details how the irreversible expansion is practically achieved.

Consider the following three types of expansions:

- (a) a reversible expansion from  $P_i$  to  $P_f = 5.0$  bar;
- (b) a single-step irreversible expansion against a constant external pressure of 5.0 bar until  $P_{\text{gas}} = P_{\text{ext}}$ ; and
- (c) a two-step irreversible expansion consisting initially of an expansion against a constant external pressure of 10.0 bar until  $P_{\text{gas}} = P_{\text{ext}}$ , followed by an expansion against a constant external pressure of 5.0 bar until  $P_{\text{gas}} = P_{\text{ext}}$ .

In each case, calculate the work done by the gas and the change of entropy of the gas for these expansions.

a) As this process is reversible, we understand the force due to the mass to gradually decrease to ensure the pressure is constant and the process is quasistatic. Further, as the process must be slow and  $F \propto V$ ,  $F = 0$ :

$$W = \int P dV \Rightarrow \begin{aligned} V_i &= 0.005 \text{ m}^3 \\ P_i &= 30 \text{ bar} = 3000000 \text{ Pa} \\ P_f &= 5 \text{ bar} = 500000 \text{ Pa} \end{aligned}$$

As the process is quasistatic:

$$\begin{aligned} PV &= nRT \\ P_i V_i &= P_f V_f \\ 0.005 \times 3000000 &= 500000 V_f \\ V_f &= 0.03 \text{ m}^3 \end{aligned}$$

$$\begin{aligned} \text{Given } W &= \int P dV \\ &= \int_{0.005}^{0.03} \frac{nRT}{V} dV \\ &= \underbrace{nRT}_{\text{constant}} \ln\left(\frac{0.03}{0.005}\right) \\ &= 3.4 nRT \text{ J} \end{aligned}$$

$$\Delta S_{\text{gas}} = \int \frac{dQ}{T}$$

$$dU = dQ + dW \quad : \quad dU = 0 \text{ as reversible}$$

$$dQ = -dW = -P dV$$

$$\begin{aligned} \Delta S_{\text{gas}} &= \frac{1}{T} \int -P dV \\ &= -\frac{1}{T} nRT \int_{0.001}^{0.03} \frac{1}{V} dV \\ &= -nR \ln\left(\frac{0.03}{0.001}\right) \\ &= -3.4 nR \text{ J/K} \end{aligned}$$

$$b) \quad P_{\text{ext}} = 5 \text{ bar} \quad : \quad P_f = 500 \text{ 000 Pa}$$

$$\begin{aligned} P_i V_i &= P_f V_f \\ \therefore V_f &= 0.03 \text{ m}^3 \quad \left( \begin{array}{l} \text{Again assuming} \\ \text{Isothermal} \end{array} \right) \end{aligned}$$

$$\begin{aligned} W &= \int_{0.001}^{0.03} P_{\text{ext}} dV \\ &= \int_{0.001}^{0.03} 500 \text{ 000 } dV \\ &= 500 \text{ 000} (0.03 - 0.001) \\ &= 14 \text{ 500 J} \end{aligned}$$

We know  $\Delta S_{\text{rev}} = \Delta S_{\text{irrev}}$   
if initial and final states are  
the same:

$$\begin{aligned} \Delta S &= \int \frac{1}{T} dQ_{\text{rev}} \\ &= \frac{1}{T} \int -P dV \\ &= \frac{1}{T} \int_{0.001}^{0.03} -\frac{nRT}{V} dV \\ &= -nR \ln\left(\frac{0.03}{0.001}\right) = 3.4 nR \end{aligned}$$

c) Two Step:

$$\begin{aligned}\text{Step 1: } V_i &= 0.001 \text{ m}^3 & P &= 3\,000\,000 \text{ Pa} \\ P_i &= 1\,000\,000 \text{ Pa} \\ \therefore V_f &= 0.003 \text{ m}^3\end{aligned}$$

$$\begin{aligned}W &= \int_{0.001}^{0.003} P_{\text{ext}} dV \\ &= \int_{0.001}^{0.003} 1\,000\,000 dV \\ &= 1099 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta S &= \int -\frac{1}{T} \frac{nRT}{V} dV \\ &= -nR \int_{0.001}^{0.003} \frac{1}{V} dV \\ &= -1.1 nR\end{aligned}$$

$$\begin{aligned}\text{Step 2: } P_i &= 1\,300\,000 \text{ Pa} & V_i &= 0.003 \\ P_f &= 500\,000 \text{ Pa} \\ \therefore V_f &= 0.006\end{aligned}$$

$$\begin{aligned}W &= \int_{0.003}^{0.006} P_{\text{ext}} dV \\ &= \int_{0.003}^{0.006} 500\,000 dV \\ &= 347 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta S &= \int \frac{dQ}{T} \\ &= -nR \int_{0.003}^{0.006} \frac{1}{V} dV \\ &= -0.69 nR\end{aligned}$$

Thus finally we find:

$$W_{\text{total}} = 1446 \text{ kJ}$$

$$\Delta S_{\text{total}} = -1.8 nR$$

**Problem 6.3 [FOR ASSIGNMENT 3; max 10 points]**

**Efficiency of the Otto cycle.**

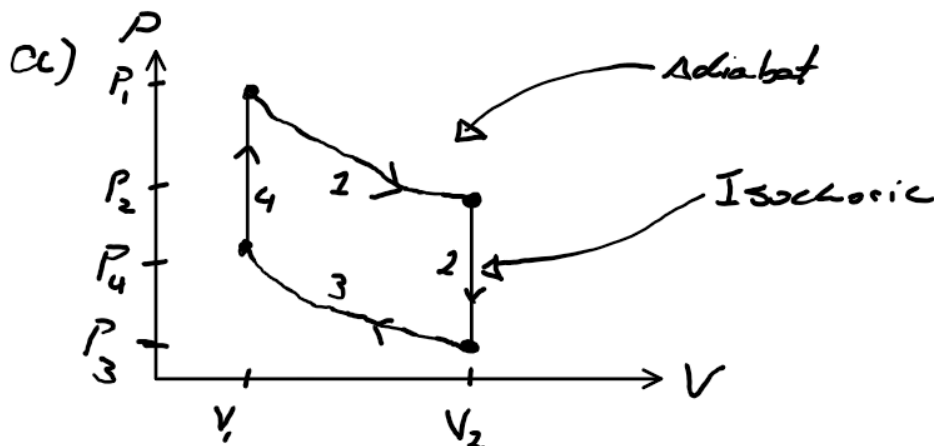
The Otto cycle is a set of processes that model the operation of the spark ignition internal combustion engine. The Otto cycle features two isochoric processes and two adiabatic processes.

- (a) Sketch a  $PV$  diagram for the Otto cycle. Include arrows to mark the direction of the cycle, and for each step indicate the sign of the changes you would expect for  $\Delta U$ ,  $Q$  and  $W$ .
- (b) Assume that the gas in the piston can be treated as an ideal gas. Show that the efficiency of the Otto cycle is

$$\epsilon = 1 - \left( \frac{V_{\min}}{V_{\max}} \right)^{\gamma-1},$$

where  $V_{\max}$  and  $V_{\min}$  are the maximum and minimum volumes achieved during the cycle, respectively, and  $\gamma$  is the adiabatic index.

- (c) Sketch the efficiency of the Otto cycle versus the compression ratio (defined as  $r = \left( \frac{V_{\max}}{V_{\min}} \right)$ ). Comment on why high compression ratios may not be feasible in practice.  
(HINT: the air-fuel mixture is injected before the start of the compression process.)



Combustion implies that the gas does work on the piston, which further implies the work calculated by the integral of a  $PV$  diagram must be net positive and thus it must be clockwise.

Stage 1: As the process is adiabatic, by definition the isolated system will have a 0J value for  $Q$ . We clearly notice that the area under this curve positive, and thus work is positive. As a result, we have a final positive  $\Delta U$  value.

Stage 2: During this isochoric process, the work is evidently 0J, however, the decrease in pressure implies a similar decrease in internal energy  $\Delta U$  and thus a negative  $Q$ .



Stage 3: This adiabatic process is similar to the first, however in the opposite direction, and thus the work is negative. This results in a negative  $\Delta U$  as  $Q$  is adiabatically 0J.

Stage 4: This final isochoric process involves an increase in pressure. As work is 0J, we understand that heat is transferred into the system, positive  $Q$  and thus  $\Delta U$  is positive.

b) We understand the efficiency of a heat engine to be:

$$\epsilon = \frac{W_{\text{net}}}{Q_{\text{in}}} = \frac{Q_h + Q_c}{Q_h} = 1 + \frac{Q_c}{Q_h}$$

We notice heat is added in stage 4 ( $Q_h$ ) and removed/lost in stage 2 ( $Q_c$ )

$$Q = \int_{T_c}^{T_h} dQ = \int_{T_c}^{T_h} mc dT$$

$$\therefore Q_h = mc(T_1 - T_4)$$

$$Q_c = mc(T_3 - T_2)$$

$$\therefore \epsilon = 1 - \frac{mc(T_3 - T_2)}{mc(T_1 - T_4)} = 1 - \frac{T_3 - T_2}{T_1 - T_4}$$

We make use of the following rules:  
① Considering the gas as ideal:

$PV = nRT$  For stage 2 and 4 we find:

$$\frac{nRT_2}{P_2} = \frac{nRT_3}{P_3} \quad \therefore \frac{T_2}{P_2} = \frac{T_3}{P_3}$$

$$\text{Similarly: } \frac{T_1}{P_1} = \frac{T_4}{P_4}$$

We can therefore make use of  $P_1 V_1^\gamma = P_2 V_2^\gamma$  can go to  $T_1 V_1^\gamma = T_2 V_2^\gamma$ . We can use this for the adiabats given  $PV^{\gamma-1} = \text{constant}$ .

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$T_3 V_2^\gamma = T_4 V_1^\gamma$$

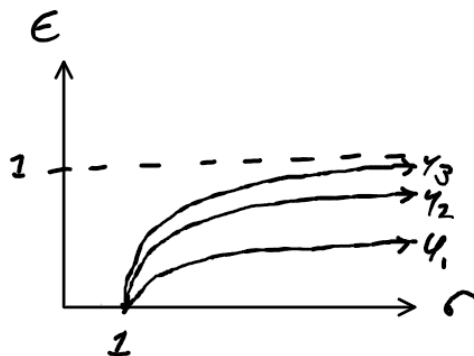
$$\therefore (T_1 - T_4) V_1^\gamma = (T_2 - T_3) V_2^\gamma \Rightarrow \frac{T_1 - T_4}{T_2 - T_3} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

$$\therefore \epsilon = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1} = 1 - \left(\frac{V_{\min}}{V_{\max}}\right)^{\gamma-1}$$

c) given the compression ratio  $r = \frac{V_{\max}}{V_{\min}}$  :

$$\epsilon = 1 - \left(\frac{1}{r}\right)^{\gamma-1} = 1 - \frac{1}{r^{\gamma-1}}$$

Generally for  $\gamma > 1$  we find the efficiency-compression ratio curve:



As can be seen in the figure, for just a few adiabatic indices, we find the curve to start at  $r = 1$  and increase to some asymptote, with the highest efficiencies being those with curves approaching  $\epsilon = 1$ . Despite the efficiency for all adiabatic indices indicating an increase as the compression ratio is increased, this limit can only go so far. The compression ratio is a direct measure of the maximum to minimum volume, and so as it increases, so too does the temperature. Significantly, as the air-fuel mixture is injected prior to compressions, if the temperature increases enough, spontaneous combustion in unwanted locations may occur without a spark. As a result, it is likely that high compression ratios will not be feasible in practice.

**Problem 6.5 [FOR ASSIGNMENT 3; max 10 points]**

**Efficiency and COP on a  $TS$  diagram.**

Figure 3 shows the operational cycle of an apparatus on a  $TS$  diagram. The cycle has the shape of a parallelogram and can operate in both directions:  $A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$  and  $D \rightarrow C \rightarrow B \rightarrow A \rightarrow D$ . The operation cycle includes a stage where heat  $Q_{\text{in}}$  is absorbed by the device and a stage when heat  $Q_{\text{out}}$  is rejected by the device.

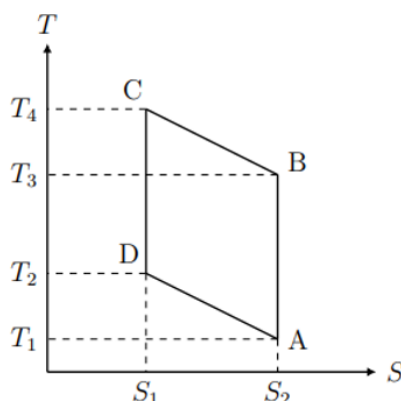


Figure 3:  $TS$  diagram of an apparatus' operational cycle. Important values are indicated.

- (a) What should the direction of the cycle in Figure 3 be if the device is supposed to work like an engine (i.e., produce useful work)?
- (b) Determine the efficiency of such an engine.
- (c) COP is defined by the ratio  $\frac{\text{benefit}}{\text{cost}}$ —for example,  $\text{COP} \equiv \frac{Q_{\text{absorbed}}}{W}$  in the case of a refrigerator. Determine the COP of the cycle in Figure 3 if the direction is reversed from part (a).
- (d) The purpose of a heat pump is to remove the heat from a cold reservoir and add this heat to a hot reservoir. Calculate the COP if the device in Figure 3 is used as a heat pump. Compare the amount of external electrical energy needed to add 1 J of heat to the hot reservoir using this heat pump, and the amount of external electrical energy required to generate 1 J of heat by using a conventional resistive heating element.

a) In order to produce useful work, the work done by the gas must be positive. We can calculate work from a  $TS$  curve as follows:  
The first law of thermodynamics gives:

$$dU = dQ - dW$$

We notice  $dQ = TdS$      $dW = PdV$

$$dU = TdS - PdV$$

For the process above, given  $\Delta U = 0$

$$0 = \oint TdS - \oint PdV$$

$$\oint PdV = \oint TdS$$

$$W = \oint TdS$$

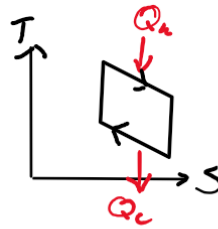
Thus work is the area enclosed by the TS curve.

So finally we conclude that the process must be clockwise in order to produce positive work (Top Integral - Bottom Integral  $> 0$ ).

b) We know:

$$E = \frac{W_{out}}{Q_h} = \frac{Q_h - Q_c}{Q_h}$$

For a TS curve:



Thus:

$$\frac{W_{out}}{Q_{in}} = \frac{(S_2 - S_1)(T_3 - T_1)}{\frac{1}{2}(S_2 - S_1)(T_4 - T_3) + (S_2 - S_1)T_3}$$

$$= \frac{T_3 - T_1}{T_4 + T_3}$$

c) Should the direction be reversed i.e.  $w = -ve$  :

$$W = \oint T dS$$

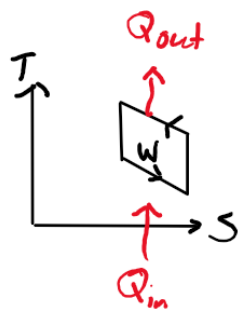
$$Q_{\text{absorbed}} = Q_{\text{in}}$$

$$\text{COP} = \frac{Q_{\text{in}}}{W} = \frac{\frac{1}{2}(S_1 - S_2)(T_4 - T_3) + (S_1 - S_2)T_3}{(S_1 - S_2)(T_3 - T_1)}$$

↙ anticlockwise

$$= \frac{T_4 + T_3}{T_3 - T_1}$$

d) If used as a heat pump:



$$\text{COP} = \frac{Q_{\text{in}}}{W} = \frac{\frac{1}{2}(T_1 - T_2)(S_2 - S_1) + (S_2 - S_1)T_1}{(S_2 - S_1)(T_3 - T_1)}$$

$$= \frac{T_1 + T_2}{T_3 - T_1}$$

Notice that for the part b engine:

$$\epsilon = \frac{T_3 - T_1}{T_4 + T_3}$$

$$\therefore \text{COP} = \frac{T_4 + T_3}{T_3 - T_1}$$

For  $IJ$  of heat transferred:

$$W = \frac{1}{\cos} J$$

For the heat pump:

$$W_P = \frac{T_3 - T_1}{T_1 + T_2} J$$

For resistive:

$$W_R = \frac{T_3 - T_1}{T_4 + T_3} J$$

$T_1 + T_2 < T_4 + T_3$   
Thus we notice that the heat pump  
is more efficient requiring a factor  
of  $\frac{T_1 + T_2}{T_4 + T_3} J$  less than the resistive  
element.