

# PHYS 143 Discussion Week 8 - Thermodynamics

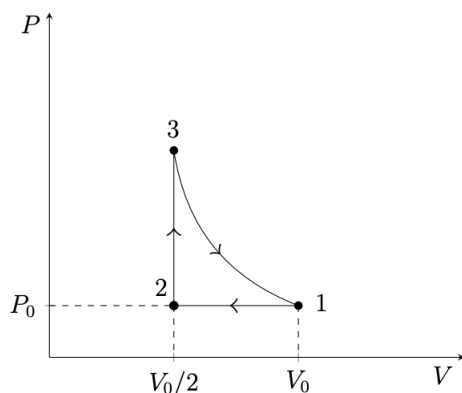
Rio Weil

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## 1 Problems

### 1.1 Heat Engine

Shown below is a 3-step heat engine, where the work medium is monoatomic gas. Step  $3 \rightarrow 1$  is isothermal.



- (a) What is the ratio of temperatures between point 3 and 1?
- (b) Solve for the pressure at point 3 in terms of  $P_0, V_0$ .
- (c) Mark the highest temperature  $T_H$  and lowest temperature  $T_C$  on the graph.
- (d) Solve for the efficiency of the heat engine, where your answer should not depend on  $P_0, V_0$ , or the amount of gas in the engine.

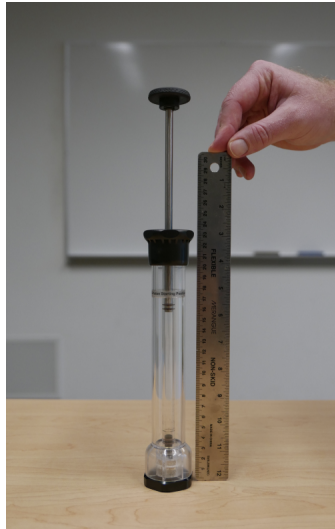
### 1.2 Carnot Efficiency From the Second Law

Using the second law of thermodynamics, prove that the that the carnot efficiency:

$$e = 1 - \frac{T_C}{T_H} \quad (1.1)$$

is the maximum attainable for *any* heat engine. To do this, consider an abstract heat engine, where it takes in heat  $Q_H$  from a hot reservoir at temperature  $T_H$ , does work  $W$ , and throws away waste heat into a cold reservoir at temperature  $T_C$ .

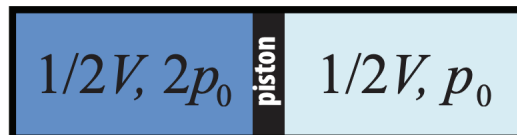
### 1.3 Adiabatic Compression



- Show that  $PV^{\frac{\gamma+2}{\gamma}}$  is a constant through an adiabatic process, using the ideal gas law  $PV = NkT$  and  $U = \frac{\gamma}{2}NkT$ .
- Suppose we have a cylinder of volume  $V_0$ , containing air at room temperature  $T_0$  and standard pressure  $P_0$  and a piece of paper with combustion temperature  $T_C$ . The cylinder contains a movable piston. We hit the piston very quickly, and at some  $V_C$  the paper combusts - at what volume does this happen?
- What is the work done on the gas (from energy conservation)?
- What is the work done on the gas (from integration)?
- Consider now a very small fractional change of the cylinder volume, from  $V$  to  $V - \delta V$ . What is the fractional change in temperature  $\frac{\delta T}{T}$  in terms of  $\frac{\delta V}{V}$  and  $\gamma$ ?
- Repeat (d) but for pressure.
- Physically, why does the temperature rise?
- Physically, why does the pressure rise? Can you reason why the fractional change of (e) greater than (d)?

### 1.4 Equilibration and Entropy

Consider an ideal monoatomic gas in a cylinder with a movable piston in the middle, separating the cylinder into two parts. The cylinder itself is an isolated system, and the two gas volumes in the cylinder are closed systems. They can exchange heat and work with one another, but no particles.



In the initial configuration,  $V_L^i = V_R^i = V/2$ . The gas pressure in the left part of the container is twice the right part,  $p_R^i = p_0, p_L^i = 2p_0$ . The temperature in both parts is  $T$ .

- (a) What is the equilibrium position of the piston? What are the temperatures when the final position is reached?
- (b) What is the change in entropy during the equilibration process?
- (c) Show that the entropy in the final configuration is a maximum as  $V_L^f$  is varied. Does this make sense?

## 2 Solutions

### 2.1 Heat Engine

- (a) Since process  $3 \rightarrow 1$  is isothermal,  $T_1 = T_3$ . So, the ratio would be 1:1.
- (b) Since  $3 \rightarrow 1$  is an isothermal process, we have that  $P_1 V_1 = P_3 V_3$ . This can then be rearranged to get that  $P_3 = 2P_0$ .
- (c) We can see from the graph that point 2 has the lowest temperature (minimized product of  $P, V$ ). Since  $3 \rightarrow 1$  is isothermal, that means that points 3, 1, and any point on the process between are at the highest temperature.
- (d) We'll start off by calculating the heat flowing into the engine. Heat must flow into the engine during processes  $2 \rightarrow 3$  (since it gains energy with no work done) and  $3 \rightarrow 1$  (since it does work but remains at the same energy). Since  $2 \rightarrow 3$  is isochoric we can say that

$$\begin{aligned}
 Q &= \Delta U \\
 &= \frac{\chi}{2} Nk \Delta T \\
 &= \frac{\chi}{2} Nk \Delta \frac{PV}{Nk} \text{ applying ideal gas law} \\
 &= \frac{\chi}{2} V_2 (P_3 - P_2) \\
 &= \frac{\chi}{2} \frac{V_0}{2} (2P_0 - P_0) \\
 &= \frac{\chi}{4} V_0 P_0
 \end{aligned} \tag{2.1}$$

Next, since process  $3 \rightarrow 1$  is isothermal we can say that

$$\begin{aligned}
 Q &= -W \\
 &= -NkT \ln \frac{V_3}{V_1} \\
 &= Nk \frac{P_1 V_1}{Nk} \ln \frac{V_1}{V_3} \\
 &= P_0 V_0 \ln \frac{V_0}{V_0/2} \\
 &= P_0 V_0 \ln 2
 \end{aligned} \tag{2.2}$$

So in total we get that  $Q_{in} = \frac{\chi}{4} V_0 P_0 + P_0 V_0 \ln 2$ . Next, we'll deal with the net work done by the system. Process  $1 \rightarrow 2$  is isobaric, so we can pretty quickly calculate that we do  $\frac{P_0 V_0}{2}$  joules of work on the system. Process  $2 \rightarrow 3$  is isochoric and does no work. Since process  $3 \rightarrow 1$  is isothermal, we can say

that  $W = -Q$ . Thus, we get that  $P_0 V_0 \ln 2$  joules of work is done on the environment. Combining these together to calculate efficiency we get

$$\begin{aligned}\eta &= \frac{W_{net}}{Q_{in}} \\ &= \frac{P_0 V_0 \ln 2 - \frac{P_0 V_0}{2}}{\frac{\chi}{4} V_0 P_0 + P_0 V_0 \ln 2} \\ &= \frac{\ln 2 - \frac{1}{2}}{\frac{\chi}{4} + \ln(2)}\end{aligned}\tag{2.3}$$

For any monoatomic gas,  $\chi = 3$ , so we get that  $\eta \approx 0.13$ .

## 2.2 Carnot Efficiency From the Second Law

let's consider the entropy of the hot reservoir, the engine, and the cold reservoir at the end of one cycle (in other words, we consider the change in entropy of the universe after one cycle). We recall that entropy is a function of state, and therefore at the end of a single cycle, the entropy of the heat engine itself must be the same as when it started. That is,  $\Delta S_{engine} = 0$  for one full cycle. By the second law of thermodynamics  $dS \geq \frac{Q}{T}$ , the entropy of the hot reservoir decreases by the amount of heat  $Q_H$  divided by its temperature  $T_H$ , so the entropy of the hot reservoir decreases by  $\Delta S_{hot} \geq \frac{-Q_H}{T_H}$ . Conversely, the cold reservoir increases in one cycle by  $\Delta S_{cold} \geq \frac{Q_C}{T_C}$  (as it receives  $Q_C$  heat at temperature  $T_C$ ). Putting these together, we obtain the change in entropy of the universe for a single cycle:

$$\Delta S_{universe} \geq \frac{Q_C}{T_C} - \frac{Q_H}{T_H}$$

Now, the second law of thermodynamics tells us that the entropy of the universe must increase (or, to phrase it another way, if we treat the two reservoirs and the heat engine as an isolated system, the entropy of the total system must increase.) This allows us to conclude that:

$$\Delta S_{universe} \geq \frac{Q_C}{T_C} - \frac{Q_H}{T_H} \geq 0\tag{2.4}$$

So we obtain the important inequality:

$$\frac{Q_C}{T_C} - \frac{Q_H}{T_H} \geq 0$$

Which we can rearrange to obtain:

$$\frac{Q_C}{Q_H} \geq \frac{T_C}{T_H}\tag{2.5}$$

Note that to derive inequality 2.5, I have made no assumptions whatsoever about what my heat engine actually looks like; this is a completely general statement, based on the amounts of heat gained/lost from the hot/cold reservoirs, and the maximum/minimum hot/cold reservoir temperatures. Now, let us consider our definition of efficiency:

$$\eta = \frac{W}{Q_H}\tag{2.6}$$

Where  $W$  is the work done by the engine (what we get out), and  $Q_H$  is the heat that we inject into the engine in one cycle from the hot reservoir (what we put in). By energy conservation, we find that:

$$W = Q_H - Q_C\tag{2.7}$$

This might look like it came out of nowhere, so let's think about it a bit further. Just like entropy, internal energy is also a function of state; the energy something has doesn't care about how that energy got there! With this consideration, since the heat engine returns to the original state at the end of one cycle, just like the entropy change of the heat engine is zero in a single cycle, so must be the total internal energy; in other words, the heat engine must have the same energy it began with. With this consideration, we realize that the sum of the work done on the system and the heat given to the system must be 0, leading to equation 2.7 above (work this out using the first law of thermodynamics if it's still unclear!). Now, we can substitute equation 2.7 into equation 2.6, giving us:

$$e = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} \quad (2.8)$$

And now applying inequality 2.5, we have:

$$1 - \frac{Q_C}{Q_H} \leq 1 - \frac{T_C}{T_H} \quad (2.9)$$

And therefore:

$$e \leq 1 - \frac{T_C}{T_H} \quad (2.10)$$

We have hence proven Carnot's theorem, and can see that for any arbitrary heat engine, the efficiency is bounded by the Carnot efficiency.

## 2.3 Adiabatic Compression

(a) As a consequence of zero heat flow, by the first law of thermodynamics we have that:

$$\Delta E = W \quad (2.11)$$

So then for an adiabatic process, we can get that:

$$W = \frac{\chi}{2} N k_b \Delta T \quad (2.12)$$

We consider an infinitesimal amount of energy change/work:

$$\begin{aligned} dE &= \delta W \\ \frac{\chi}{2} N k_b dT &= -PdV \end{aligned} \quad (2.13)$$

We make a substitution with ideal gas law, namely

$$N k_b dT = d(PV) \quad (2.14)$$

We use that  $d(PV) = VdP + PdV$  by product rule. Making all of these substitutions gives

$$\frac{\chi}{2} (VdP + PdV) = -PdV \quad (2.15)$$

At this point you have all the parts necessary to rearrange this equation into

$$\frac{\chi}{2} \frac{dP}{P} = -\left(\frac{\chi}{2} + 1\right) \frac{dV}{V} \quad (2.16)$$

Integrating this:

$$\int_{P_1}^{P_2} \frac{\chi}{2} \frac{dP}{P} = \int_{V_1}^{V_2} -\left(\frac{\chi}{2} + 1\right) \frac{dV}{V} \quad (2.17)$$

Again, we can factor out the constant terms to get:

$$\frac{\chi}{2} \int_{P_1}^{P_2} \frac{dP}{P} = - \left( \frac{\chi}{2} + 1 \right) \int_{V_1}^{V_2} \frac{dV}{V} \quad (2.18)$$

Now evaluating the integral:

$$\frac{\chi}{2} \ln \left( \frac{P_2}{P_1} \right) = - \left( \frac{\chi}{2} + 1 \right) \ln \left( \frac{V_2}{V_1} \right) \quad (2.19)$$

Multiplying both sides of this equation by  $\frac{2}{\chi}$  yields:

$$\ln \left( \frac{P_2}{P_1} \right) = - \left( \frac{\chi + 2}{\chi} \right) \ln \left( \frac{V_2}{V_1} \right) \quad (2.20)$$

We then take the natural exponent of both sides of the equation to get:

$$\begin{aligned} e^{\ln \left( \frac{P_2}{P_1} \right)} &= e^{- \left( \frac{\chi + 2}{\chi} \right) \ln \left( \frac{V_2}{V_1} \right)} \\ \frac{P_2}{P_1} &= e^{\ln \left( \left( \frac{V_2}{V_1} \right)^{- \left( \frac{\chi + 2}{\chi} \right)} \right)} \\ \frac{P_2}{P_1} &= \left( \frac{V_2}{V_1} \right)^{- \left( \frac{\chi + 2}{\chi} \right)} \end{aligned} \quad (2.21)$$

Raise both sides to the exponent -1, rearrange a bit, and you get:

$$P_1 V_1^{\frac{\chi + 2}{\chi}} = P_2 V_2^{\frac{\chi + 2}{\chi}} \quad (2.22)$$

And we can call  $\gamma = \frac{\chi + 2}{\chi}$ .

- (b) Since we hit the piston quickly the process is adiabatic, and thus it holds that  $PV^\gamma = \text{Const.}$  where for diatomic gases (air is composed of nitrogen/oxygen)  $\gamma = \frac{\chi + 2}{\chi} = \frac{7}{5}$ . Using the ideal gas law  $PV = NkT$  we can rewrite this as:

$$TV^{\gamma - 1} = \text{Const.} \quad (2.23)$$

And hence  $V_C/V_0 = (T_0/T_C)^{\frac{1}{\gamma - 1}}$  and so:

$$V_C = V_0 \left( \frac{T_0}{T_C} \right)^{\frac{5}{2}} \quad (2.24)$$

- (c) By energy conservation, since no heat is transferred between the cylinder and the surroundings, the work is given by the change in internal energy of the gas. The gas has  $N = \frac{P_0 V_0}{k_B T_0}$  molecules, so the work is given by:

$$W = \Delta E = Nk_B C_V \Delta T = \frac{5}{2} k_B \frac{P_0 V_0}{k_B T_0} (T_C - T_0) = \boxed{\frac{5}{2} P_0 V_0 \left( \frac{T_C}{T_0} - 1 \right)} \quad (2.25)$$

- (d) The work done is:

$$\begin{aligned} W &= - \int_{V_0}^{V_C} P(V) dV = - \int_{V_0}^{V_C} \frac{P_0 V_0^\gamma}{V^\gamma} dV = - P_0 V_0^\gamma \int_{V_0}^{V_C} V^{-\gamma} dV = - \frac{P_0 V_0^\gamma}{\gamma - 1} V^{1-\gamma} \Big|_{V_1}^{V_2} = \frac{P_0 V_0}{\gamma - 1} \left( \left( \frac{V_C}{V_0} \right)^{1-\gamma} - 1 \right) \\ &= \boxed{\frac{5}{2} P_0 V_0 \left( \frac{T_C}{T_0} - 1 \right)} \end{aligned} \quad (2.26)$$

(e) We give two derivations. The first uses the given formula (twice), the second a clever derivative.

*Derivation 1:* Since  $TV^{\gamma-1}$  remains constant for an adiabatic process, for initial temperature/volume  $T_1, V_1$  and final temperature/volume  $T_2, V_2$  we have that:

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \quad (2.27)$$

We have that  $T_1 = T$ ,  $V_1 = V$ ,  $T_2 = T + \delta T$  (temperature increases in adiabatic compression) and  $V_2 = V - \delta V$ , so substituting these in we have:

$$TV^{\gamma-1} = (T + \delta T)(V - \delta V)^{\gamma-1}. \quad (2.28)$$

Now factoring out  $T$  and  $V^{\gamma-1}$  from the RHS we have:

$$TV^{\gamma-1} = TV^{\gamma-1} \left(1 + \frac{\delta T}{T}\right) \left(1 - \frac{\delta V}{V}\right)^{\gamma-1} \quad (2.29)$$

so cancelling terms we get:

$$1 = \left(1 + \frac{\delta T}{T}\right) \left(1 - \frac{\delta V}{V}\right)^{\gamma-1}. \quad (2.30)$$

As the piston is pushed inwards a small distance,  $\delta V$  is small and hence,  $\delta V/V \ll 1$ . Hence we can apply the suggested binomial approximation to get:

$$1 \approx \left(1 + \frac{\delta T}{T}\right) \left(1 - (\gamma - 1) \frac{\delta V}{V}\right) \quad (2.31)$$

We can now isolate  $\delta T/T$  to obtain:

$$\frac{\delta T}{T} \approx \left(1 - (\gamma - 1) \frac{\delta V}{V}\right)^{-1} - 1 \quad (2.32)$$

Again using that  $\delta V/V \ll 1$ , we can apply the suggested formula a second time to obtain:

$$\frac{\delta T}{T} \approx \left(1 - (-1)(\gamma - 1) \frac{\delta V}{V}\right) - 1 \quad (2.33)$$

Hence we obtain the result:

$$\frac{\delta T}{T} \approx (\gamma - 1) \frac{\delta V}{V} \quad (2.34)$$

and putting in  $\gamma = 5/3$  we have:

$$\boxed{\frac{\delta T}{T} \approx \frac{2}{3} \frac{\delta V}{V}} \quad (2.35)$$

*Derivation 2:* We start with  $TV^{\gamma-1} = C$  for some constant  $C$ . Taking the derivative of this equation and using the product and chain rule, we have:

$$dT \cdot V^{\gamma-1} + T(\gamma - 1)V^{\gamma-2}dV = 0 \quad (2.36)$$

Dividing out by  $TV^{\gamma-1}$  we obtain:

$$\frac{dT}{T} + (\gamma - 1) \frac{dV}{V} = 0 \quad (2.37)$$

Rearranging we have:

$$\frac{dT}{T} = -(\gamma - 1) \frac{dV}{V} \quad (2.38)$$

And letting  $dT = \delta T$ ,  $dV = -\delta V$  (the volume decreases), we obtain:

$$\frac{\delta T}{T} \approx (\gamma - 1) \frac{\delta V}{V} \quad (2.39)$$

and again with  $\gamma = 5/3$  we have:

$$\boxed{\frac{\delta T}{T} \approx \frac{2}{3} \frac{\delta V}{V}} \quad (2.40)$$

in agreement with (2.35).

- (f) Using an identical argument as (d) (either the binomial approximation or the derivative method) works. To see this, note that  $PV^\gamma$  is constant in a fast adiabatic process, of nearly identical form to  $TV^{\gamma-1}$ , just by substituting  $T$  for  $P$  and  $\gamma - 1$  for  $\gamma$ . Hence we can just make this substitution into our final result in (2.34) to obtain:

$$\boxed{\frac{\delta P}{P} \approx \gamma \frac{\delta V}{V} = \frac{5}{3} \frac{\delta V}{V}} \quad (2.41)$$

- (g) Molecules that hit the piston gain velocity, and hence the average kinetic energy (and therefore temperature) of the gas increases.
- (h) Molecules that hit the piston gain velocity and collisions increase in frequency, raising average force against container walls and hence pressure. The fractional change is greater for pressure than for temperature, as we have two factors contributing to increase in pressure.

## 2.4 Equilibration and Entropy

- (a) The temperature is uniform after equilibration. Since the cylinder is isolated, its total energy is conserved, and therefore the final temperature equals the initial temperature:

$$\boxed{T_L^f = T_R^f = T} \quad (2.42)$$

The equilibrium position is reached when the pressure  $p_L$  on the left equals the pressure  $p_R$  on the right, so by the ideal gas law (noting that  $N_L k_B T$ ,  $N_R k_B T$  are constant through the evolution):

$$p_L^f V_L^f = p_L^i V_L^i = p_0 V \quad (2.43)$$

$$p_R^f V_R^f = p_R^i V_R^i = p_0 B/2 \quad (2.44)$$

at equilibrium  $p_L^f = p_R^f$  and so  $V_L^f / V_R^f = 2$ . Furthermore,  $V_L^f + V_R^f = V$ , so:

$$\boxed{V_L^f = \frac{2}{3} V, V_R^f = \frac{1}{3} V} \quad (2.45)$$

- (b) The entropy change is:

$$\Delta S = N_L k_B \ln\left(\frac{V_L^f}{V_L^i}\right) + N_R k_B \ln\left(\frac{V_R^f}{V_R^i}\right) + \frac{3}{2} N_L k_B \ln\left(\frac{T_L^f}{T_L^i}\right) + \frac{3}{2} N_R k_B \ln\left(\frac{T_R^f}{T_R^i}\right) \quad (2.46)$$

Since  $T^f = T^i = T$  for both sides the temperature terms drop out, and from the ideal gas law:

$$N_L = \frac{P_0 V}{k_B T}, N_R = \frac{P_0 B}{2 k_B T} \quad (2.47)$$



so using the  $V^f$  from part (a):

$$\Delta S = \frac{P_0 V}{T} \ln\left(\frac{\frac{2}{3}V}{\frac{V}{2}}\right) + \frac{P_0 V}{2T} \ln\left(\frac{\frac{1}{3}V}{\frac{V}{2}}\right) = \frac{P_0 V}{2T} \left( \ln\left(\left(\frac{4}{3}\right)^2\right) + \ln\left(\frac{2}{3}\right) \right) = \boxed{\frac{P_0 V}{2T} \ln\left(\frac{32}{27}\right)} \quad (2.48)$$

(c) Let us denote  $V_L^f$  as  $v$  and express the final entropy as a function of  $v$ , and  $K = \frac{P_0 V}{2T}$  then:

$$S^f = S^i + \Delta S = S^i + 2K \ln\left(\frac{v}{\frac{V}{2}}\right) + K \ln\left(\frac{V-v}{V/2}\right) \quad (2.49)$$

Then:

$$\frac{dS^f}{dv} = 2K \frac{1}{v} - K \frac{1}{V-v} \quad (2.50)$$

Setting this to zero, we find:

$$\frac{dS^f}{dv} = 0 \implies v = \frac{2V}{3} \quad (2.51)$$

Which tells us that  $V_L^f = \frac{2}{3}V$  is an extremum, and furthermore:

$$\left. \frac{d^2 S^f}{dv^2} \right|_{v=2V/3} = -\frac{27}{2} \frac{K}{V^2} < 0 \quad (2.52)$$

so the final entropy is maximized there.