

Mon: Candidate.

Tues: HW Read 2.21

Heat engines

A heat engine converts heat into useful work. The heat engine uses a thermodynamic system as an intermediary to do the conversion and to illustrate the process we consider the situation where the intermediary is an ideal gas. The heat engine:

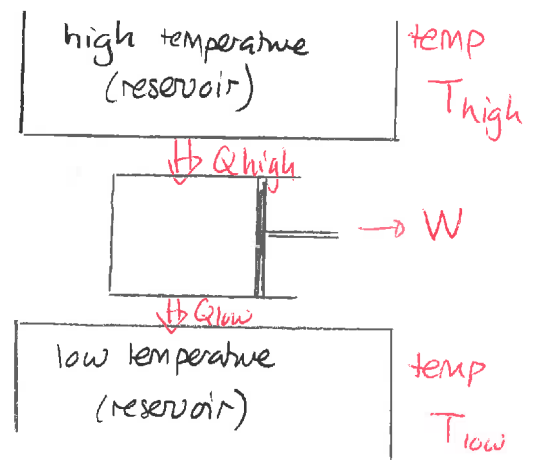
- 1) operates in a cycle so that at the end of a cycle the state of the gas returns to what it was at the beginning of the cycle.
- 2) during the cycle it absorbs heat from its environment which must be at a higher temperature than the gas.
- 3) during the cycle it ejects heat into its environment which must be at a lower temperature than the gas.

Let

$W$  = magnitude of work done by gas in one cycle

$Q_{high}$  = heat entering gas in one cycle

$Q_{low}$  = heat leaving gas in one cycle



Then the first law of thermodynamics states that, for the gas,

$$\Delta E = Q + W_{\text{on gas}}$$

$\rightarrow 0 = Q_{\text{high}} - Q_{\text{low}} - W$   $\leftarrow$  by gas  
since at end of  
cycle  $E = \text{same as at beginning}$ .

Thus:

$$W = Q_{\text{high}} - Q_{\text{low}}$$

Then the efficiency of the gas is

$$\eta = \frac{W}{Q_{\text{high}}} = \frac{Q_{\text{high}} - Q_{\text{low}}}{Q_{\text{high}}}$$

$$\Rightarrow \boxed{\eta = 1 - \frac{Q_{\text{low}}}{Q_{\text{high}}}}$$

We can now ask whether, given two reservoirs at two fixed temperatures, there are any fundamental limits on the efficiency of an ideal gas heat engine.

## 1 Heat engine between two baths

A heat engine operates between a bath at a high temperature  $T_{\text{high}}$  and another bath at a low temperature  $T_{\text{low}}$ . The efficiency of the engine is

$$\eta = 1 - \frac{Q_{\text{low}}}{Q_{\text{high}}}$$

Apply the second law to this situation to determine an expression for the efficiency solely in terms of the temperatures.

Answer:  $\Delta S_{\text{tot}} = \Delta S_{\text{engine}} + \Delta S_{\text{high res}} + \Delta S_{\text{low res}} \geq 0$

The entropy of the engine only depends on the state of the gas. Since the gas operates in a cycle  $\Delta S_{\text{engine}} = 0$

Each bath operates at fixed temperature. Thus

$$\Delta S_{\text{high res}} = - \frac{Q_{\text{high}}}{T_{\text{high}}} \quad \text{\color{red} } \text{leaves bath}$$

$$\Delta S_{\text{low res}} = \frac{Q_{\text{low}}}{T_{\text{low}}} \quad \text{\color{red} } \text{enters bath}$$

so  $0 + \left( - \frac{Q_{\text{high}}}{T_{\text{high}}} \right) + \frac{Q_{\text{low}}}{T_{\text{low}}} \geq 0$

$$\Rightarrow \frac{Q_{\text{low}}}{T_{\text{low}}} \geq \frac{Q_{\text{high}}}{T_{\text{high}}} \quad \Rightarrow \frac{Q_{\text{low}}}{Q_{\text{high}}} \geq \frac{T_{\text{low}}}{T_{\text{high}}}$$

$$\Rightarrow 1 - \frac{Q_{\text{low}}}{Q_{\text{high}}} \leq 1 - \frac{T_{\text{low}}}{T_{\text{high}}}$$

$$\Rightarrow \eta \leq 1 - \frac{T_{\text{low}}}{T_{\text{high}}}$$

Thus the first and second laws of thermodynamics predict

Suppose that a heat engine operates between two reservoirs, one at temperature  $T_{\text{high}}$ , the other at temperature  $T_{\text{low}}$ , so that  $T_{\text{low}} < T_{\text{high}}$ . Then the efficiency of the heat engine is bounded by:

$$\eta_{\text{max}} = 1 - \frac{T_{\text{low}}}{T_{\text{high}}}$$

In the previous example we have  $\eta = 0.21$  and  $T_{\text{low}} = 300\text{K}$  and  $T_{\text{high}} = 900\text{K}$ . So the maximum efficiency is  $\eta = 1 - \frac{300}{900} = \frac{2}{3}$ .

Is there some cycle that attains this?

### Carnot cycle

It will emerge that there is a cycle in which an ideal gas can attain the maximum possible efficiency. We want the heat exchanges with the two reservoirs to satisfy

$$\Delta S_{\text{total}} = \Delta S_{\text{engine}} + \Delta S_{\text{high res}} + \Delta S_{\text{low res}} = 0$$

The cycle which accomplishes this is called the Carnot cycle.

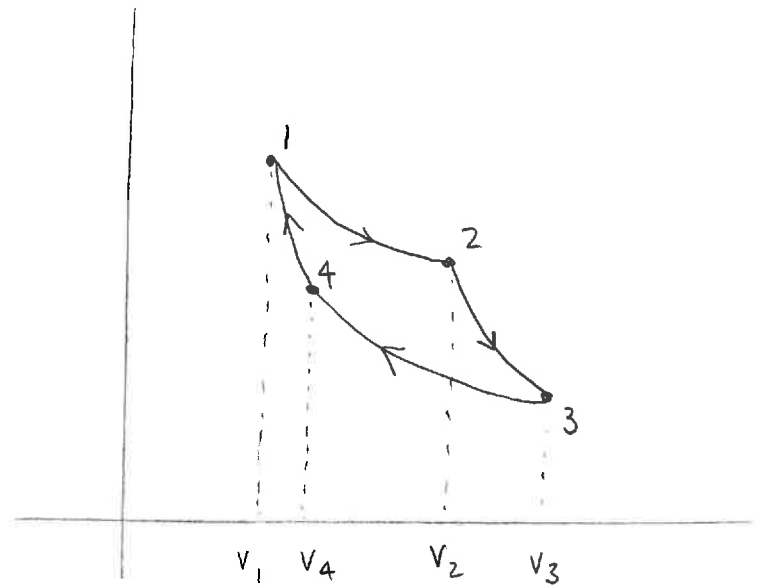
There are four stages

I (1→2) isothermal expansion at high temp.

II (2→3) adiabatic expansion

III (3→4) isothermal compression at low temp

IV (4→1) adiabatic compression.



We analyze this using

1) Ideal gas law  $PV = NkT$

2) Ideal gas energy  $E = \frac{3}{2}NkT$

3) adiabatic process:  $PV^\gamma = \text{constant}$

4) first law of thermodynamics

## 2 Carnot cycle

Consider the Carnot cycle as described in class.

- a) Using the fact that for an isothermal process  $PV$  is constant and that for an adiabatic process  $PV^\gamma$  is constant, relate the pressures and volumes at the junctions of the cycle. Successively eliminate the pressures to show that

$$\frac{V_4}{V_3} = \frac{V_1}{V_2}.$$

- b) Show that

$$\frac{Q_{\text{low}}}{Q_{\text{high}}} = \frac{T_{\text{low}}}{T_{\text{high}}}.$$

- c) Determine an expression for the efficiency of the Carnot cycle.

Answer:

a)	Stage I	Isothermal	$P_1 V_1 = P_2 V_2$	$\Rightarrow P_2 = P_1 \frac{V_1}{V_2}$
	Stage II	Adiab.	$P_2 V_2^\gamma = P_3 V_3^\gamma$	$\Rightarrow P_3 = P_2 \left(\frac{V_2}{V_3}\right)^\gamma$
	Stage III	Isothermal	$P_3 V_3 = P_4 V_4$	$\Rightarrow P_4 = P_3 \left(\frac{V_3}{V_4}\right)$
	Stage IV	Adiab.	$P_4 V_4^\gamma = P_1 V_1^\gamma$	$\Rightarrow P_1 = P_4 \left(\frac{V_4}{V_1}\right)^\gamma$

$$\begin{aligned} \text{So } P_1 &= P_3 \left(\frac{V_3}{V_4}\right) \left(\frac{V_4}{V_1}\right)^\gamma \\ &= P_2 \left(\frac{V_2}{V_3}\right)^\gamma \left(\frac{V_3}{V_4}\right) \left(\frac{V_4}{V_1}\right)^\gamma \\ &= P_1 \left(\frac{V_1}{V_2}\right) \left(\frac{V_2}{V_3}\right)^\gamma \left(\frac{V_3}{V_4}\right) \left(\frac{V_4}{V_1}\right)^\gamma \end{aligned}$$

$$\Rightarrow 1 = V_1^{1-\gamma} V_2^{\gamma-1} V_3^{1-\gamma} V_4^{\gamma-1}$$

$$\Rightarrow 1 = \left(\frac{V_2 V_4}{V_1 V_3}\right)^{\gamma-1}$$

$$\Rightarrow \frac{V_2 V_4}{V_1 V_3} = 1 \quad \Rightarrow \quad \frac{V_4}{V_3} = \frac{V_1}{V_2}$$

b) The first law gives

$$\Delta E = Q + W \Rightarrow Q = \Delta E - W$$

Along isothermals  $\Delta E = 0$  since

$T$  is constant.

We only need the heats and thus

the work along I and III.

	$\Delta E$	$Q$	$W$
Stage I	0	$Q_I$	$W_I = -Q_I$
Stage II	$\Delta E_{II}$	0	$W_{II}$
III	0	$Q_{III}$	$W_{III} = -Q_{III}$
IV	$\Delta E_{IV}$	0	$W_{IV}$

Stage I

$$W_I = - \int_I P dV$$

$$P = \frac{NkT_{high}}{V}$$

$$= -NkT_{high} \int_{V_1}^{V_2} \frac{dV}{V} = -NkT_{high} \ln\left(\frac{V_2}{V_1}\right) \Rightarrow Q_I = NkT_{high} \ln\left(\frac{V_2}{V_1}\right)$$

Stage III

$$W_{III} = - \int_{III} P dV = -NkT_{low} \int_{V_3}^{V_4} \frac{dV}{V}$$

$$= -NkT_{low} \ln\left(\frac{V_4}{V_3}\right) = NkT_{low} \ln\left(\frac{V_3}{V_4}\right)$$

$$\Rightarrow Q_{III} = -NkT_{low} \ln\left(\frac{V_3}{V_4}\right)$$

But  $Q_{high} = Q_I = NkT_{high} \ln\left(\frac{V_2}{V_1}\right)$

$Q_{low} = -Q_{III} = NkT_{low} \ln\left(\frac{V_3}{V_4}\right)$

so

$$\frac{Q_{low}}{Q_{high}} = \frac{NkT_{low}}{NkT_{high}} \ln\left(\frac{V_2}{V_1}\right) / \ln\left(\frac{V_3}{V_4}\right) = 1$$

$$\Rightarrow \frac{Q_{low}}{Q_{high}} = \frac{T_{low}}{T_{high}}$$

c)  $\eta = 1 - \frac{Q_{low}}{Q_{high}} = 1 - \frac{T_{low}}{T_{high}}$

Thus:

For the Carnot cycle

$$\eta = 1 - \frac{T_{low}}{T_{high}}$$

and thus the Carnot cycle attains the optimal efficiency between these reservoirs

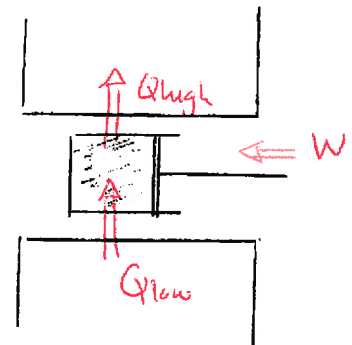
### Refrigerator

A refrigerator is a device which removes heat from a low temperature reservoir and deposits it in a higher temperature reservoir.

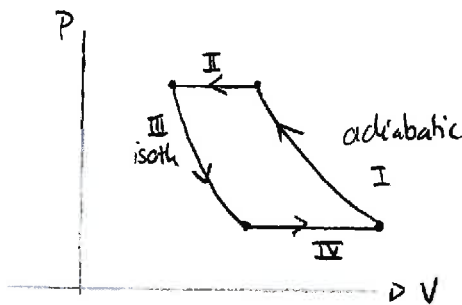
This will require work from an external source.

We could realize by various cycles.

One example is illustrated below



$$1^{st} \text{ law} \Rightarrow Q_{low} + W = Q_{high}$$



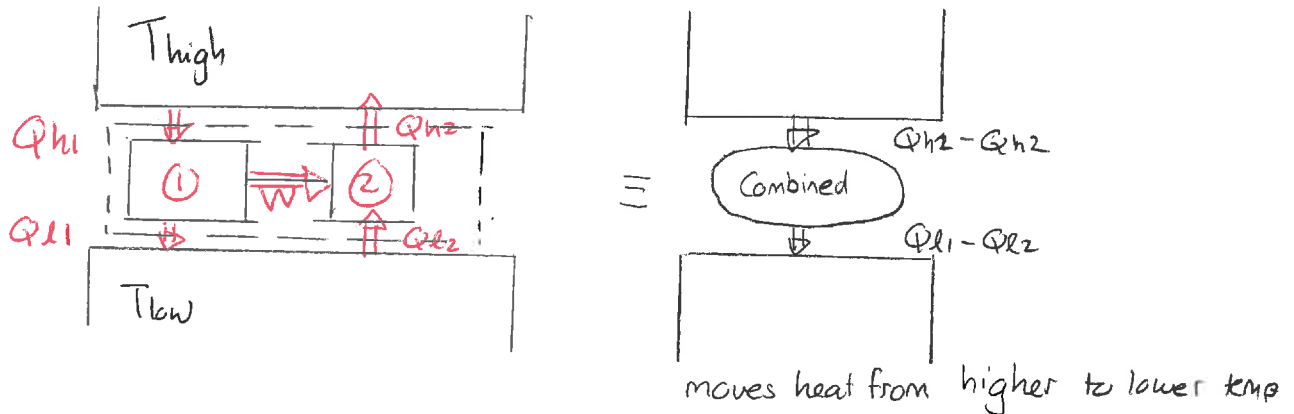
Then along the stages:

	$\Delta E$	$W_{on}$	$Q$	
I	+	+	0	temp increases
II	-	+	-	heat released to atmosphere
III	same	-	+	absorbs heat from compartment
IV	+	-	+	absorbs heat " "



## Connected engines

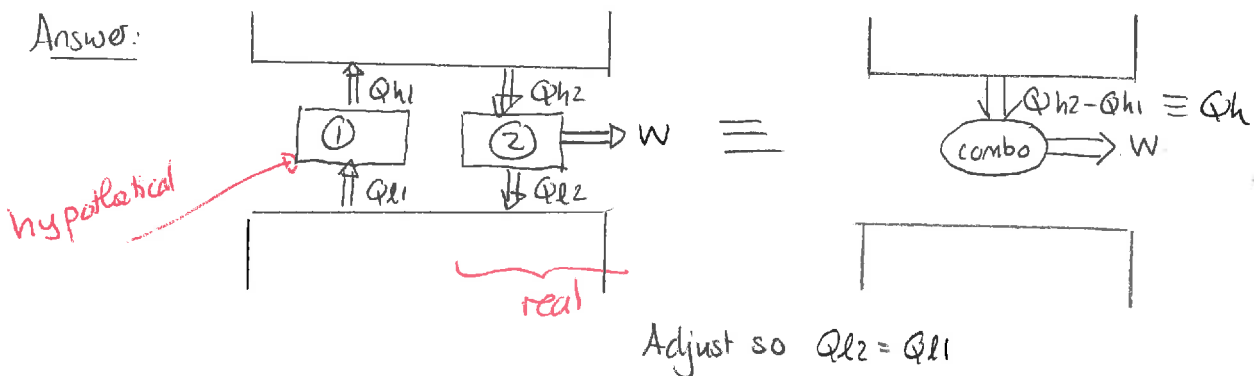
We could connect two or more engines to create a combined simple engine. Consider an example where the work output from a heat engine is used to drive a refrigerator.



We can check on a hypothetical engine

Example Suppose that a heat engine exists that can transfer heat from a low to high temperature reservoir without requiring work. Show that this can produce an engine with efficiency 1 regardless of the reservoirs

Answer:



$$\begin{aligned} \text{Here } Q_{c1} &= Q_{h1} \\ Q_{h2} &= Q_{c2} + W \end{aligned} \Rightarrow Q_{h2} - Q_{h1} = \cancel{Q_{c2}} - \cancel{Q_{h1}} + W = 0 \quad \begin{array}{l} \text{0 by setting} \\ Q_h = W \\ \text{combo} \end{array}$$

$$\text{So the efficiency of the combination is } \frac{W}{Q_h} = 1 > 1 - \frac{T_l}{T_h}$$

This is impossible

## Equivalence of the ideal gas temperature and the thermodynamic temperature.

The ideal gas temperature corresponds to that which was historically used to calibrate thermometers, and is defined via the ideal gas law  $PV = NkT$ .

Alternatively the thermodynamic temperature of a system is defined via the entropy

$$T_{th} := \frac{1}{\left(\frac{\partial S}{\partial E}\right)_{V,N}}$$

Using this we get

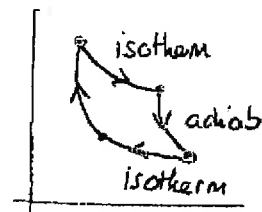
$$dE = T_{th} dS - PdV + \mu dN$$

and then the heat flow is

$$\delta Q = T_{th} dS$$

We would like to show that these are equivalent and can do this by considering a Carnot cycle. The previous analysis showed that

$$\frac{Q_h}{Q_c} = \frac{T_h}{T_c}$$



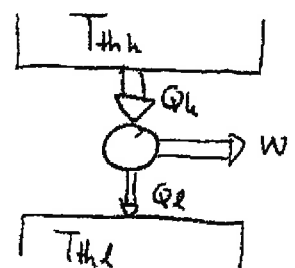
where the temperatures are ideal gas law temperatures

Now consider the engine operating between two baths at the thermodynamic temperatures  $T_{th}$  and  $T_{tl}$ . Then for the

Carnot cycle the total entropy

$$S = S_h + S_l + S_{engine}$$

satisfies  $\Delta S = 0 \Rightarrow \Delta S_h + \Delta S_l = 0$



But for a bath  $Q = \int T_{th, bath} dS \Rightarrow Q = T_{th, bath} \Delta S$

Thus 
$$\Delta S_h = - \frac{Q_h}{T_{th, h}}$$

$$\Delta S_l = \frac{Q_l}{T_{th, l}}$$

gives

$$-\frac{Q_h}{T_{th, h}} + \frac{Q_l}{T_{th, l}} = 0$$

which implies

$$\frac{Q_h}{Q_l} = \frac{T_{th, h}}{T_{th, l}}$$

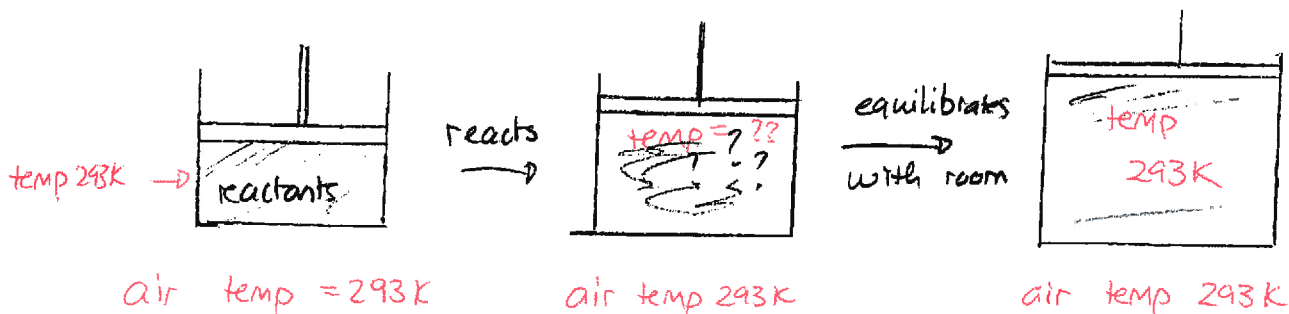
Comparing the two gives

$$\underbrace{\frac{T_{th, h}}{T_{th, l}}}_{\text{thermodynamic}} = \underbrace{\frac{T_h}{T_l}}_{\text{ideal gas}}$$

This does not immediately imply that  $T_{th} = T$  since say  $T_{th} = 3T$  would satisfy the above rule. But we can fix any multiplier to 1 to equate the two scales. Then we get that the scales are the same.

## Thermodynamic processes for systems plus baths

Consider a thermodynamic process such as a chemical reaction in a container in contact with the surrounding air



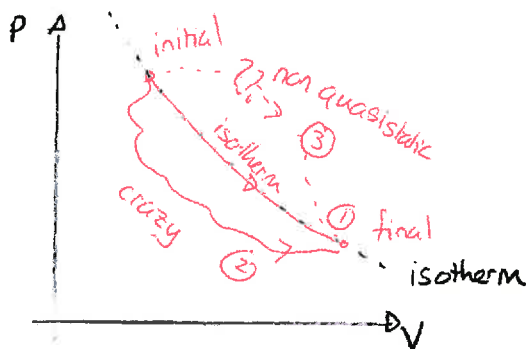
In such a reaction the system will do work on the surroundings. We would like to determine

- work done by the system on the surroundings given that the system's initial and final temperatures are the same.

We note that the system is in contact with a bath. Then the following considerations are crucial

- any heat absorbed / produced by the system is absorbed / produced by the bath.
- during this process the bath temperature stays constant

Note that the system can undergo many processes that satisfy this: The process followed by the system does not need to be isothermal. We want.



A quantity that only depends on the state of the system that bounds any possible work done by the system.