

Lecture 8 – Heat & work

LAST TIME: Recall the thermodynamic identity

$$dU = TdS - pdV \quad \text{2 ways to transfer energy between systems}$$

\uparrow
heat

\uparrow
work

TODAY: Heat and work

Heat: $dQ \equiv TdS$

Work: $dW \equiv -pdV$ (specifically “mechanical” work done on system)

(We’ll explain what d symbol means later)

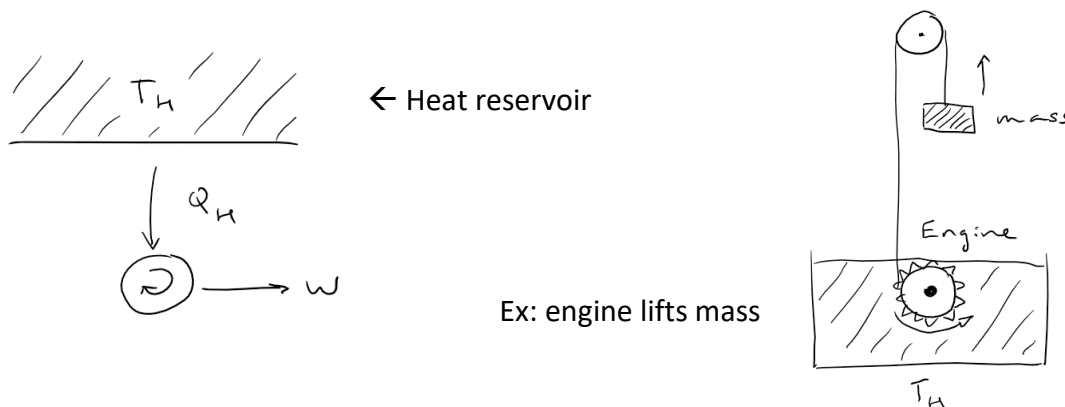
1st law of thermodynamics (conservation of energy): $dU = dQ + dW$

We separate these two types of energy transfer because they have different properties

- Work – all types of work can be interconverted. For example, an ideal electrical motor can in principle convert electrical work entirely into mechanical work
- Heat – conversely, heat cannot be completely converted into work (but work can be completely converted to heat!). This is a consequence of the 2nd law: $\Delta S \geq 0$, the total entropy of the system can never decrease.

KEY CONCEPT: Heat engine

Consider a device that continuously converts heat into work – a heat engine. Engine goes through a cycle which returns it to its original state every time, i.e. $\Delta U = 0$.



During each cycle, heat Q_H goes in, work W done, returns engine to same macrostate: $U_{\text{before}} = U_{\text{after}}$

By 1st law: $Q_H = W$

What about entropy? Consider the total closed system = reservoir + engine + mass:

$$\Delta S_{tot} = \Delta S_{res} + \Delta S_{eng} + \Delta S_{mass}$$

Reservoir loses heat each cycle so $\Delta S_{res} = -Q_H/T_H < 0$

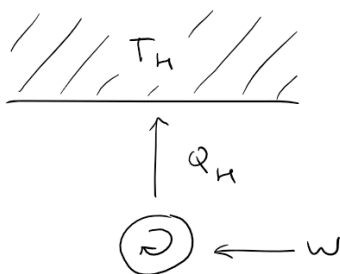
Engine returns to same state so $\Delta S_{eng} = 0$

Mass lifted but entropy does not change so $\Delta S_{mass} = 0$

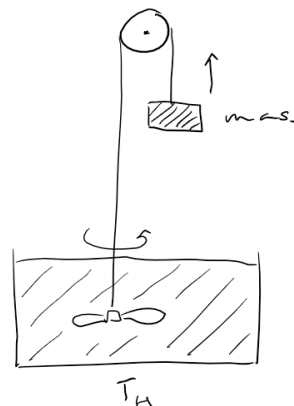
$$\Delta S_{tot} < 0 \quad \text{Violates the 2nd law of thermodynamics!}$$

So it's not possible to convert all Q into W because the entropy of the total closed system would have to decrease

Notice the reverse process is fine:

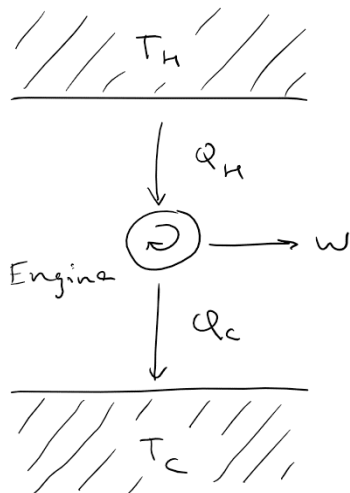


Ex: mass rotates propeller



Here $\Delta S_{tot} > 0$

So how do you build a heat engine? Entropy removed from heat reservoir must be put back into the system: a 2nd reservoir



$$1^{\text{st}} \text{ law: } Q_H = Q_C + W$$

$$2^{\text{nd}} \text{ law: } \Delta S_{tot} \geq 0$$

$$\begin{aligned} \Delta S_{tot} &= \Delta S_{H,res} + \Delta S_{C,res} \\ &= -\frac{Q_H}{T_H} + \frac{Q_C}{T_C} \end{aligned}$$

Since $Q_H > Q_C$, can only have $\Delta S_{tot} \geq 0$ for $T_H > T_C$, so H reservoir is hot, C reservoir is cold.

Define efficiency $\eta = \frac{W}{Q_H}$, i.e. how much of the heat removed can be converted to work.

$$\eta = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

Question 1: What is the maximum possible efficiency that can be achieved? Write answer in terms of T_C and T_H .

The best we can do is to put back all the entropy removed from the H reservoir into the C reservoir, so that $\Delta S_{tot} = 0$:

$$\Delta S_{tot} = -\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0.$$

So $\frac{Q_C}{Q_H} = \frac{T_C}{T_H}$, and $\eta_{max} = \eta_C = 1 - \frac{T_C}{T_H}$, which is called the Carnot efficiency.

This is the highest possible efficiency for a heat engine.

Ex: in power plant steam turbines $T_H \approx 600K$ and $T_C \approx 300K$, so $\eta_C \approx 50\%$ (in practice 40%)

$$\eta_C \rightarrow 1 \text{ only when } \frac{T_C}{T_H} \rightarrow 0$$

In practice, $\Delta S_{tot} > 0$ because additional entropy is created during cycle

$$\Delta S_{H,res} = -\frac{Q_H}{T_H} \text{ and } \Delta S_{C,res} = \frac{Q_C}{T_C} + \Delta S_{irr}$$

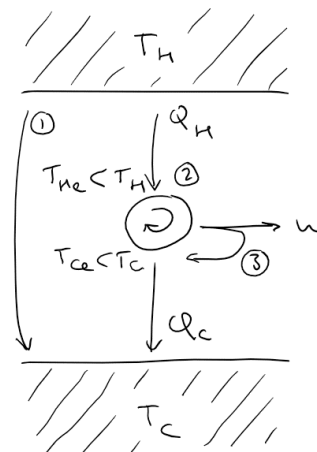
$$\Delta S_{tot} = -\frac{Q_H}{T_H} + \frac{Q_C}{T_C} > 0, \text{ so } \frac{Q_C}{Q_H} > \frac{T_C}{T_H} \text{ and}$$

$$\eta = 1 - \frac{Q_C}{Q_H} < 1 - \frac{T_C}{T_H} = \eta_C$$

Where does extra entropy change come from?

Example sources:

1. Heat bypass – heat transferred directly between H and C
2. Thermal resistance – temperature drops between H and engine, between engine and C
3. Friction loss – part of W converted to heat by friction
4. Irreversible gas expansion – will discuss at the end of lecture



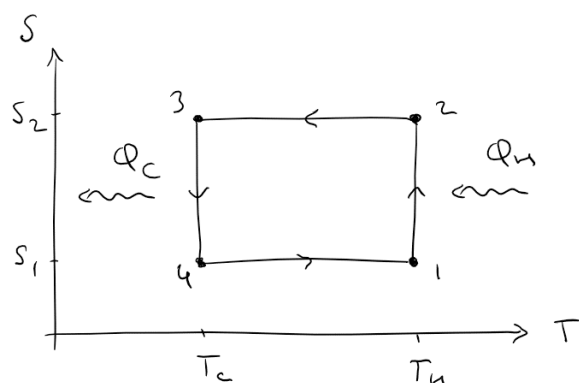
All these sources are irreversible – once entropy is created it cannot be removed without violating 2nd law

KEY CONCEPT: Carnot cycle

How does one realize a heat engine cycle with $\eta = \eta_c$?

Every engine uses a “working substance” (e.g. a gas) to absorb and expel heat and do work (e.g. by compression/expansion, moving a piston)

The Carnot cycle is between 4 macrostates (no irreversible processes)



- 1 → 2: engine takes in Q_H at constant temperature T_H (isothermal)
- 2 → 3: engine cools at constant entropy to T_C (isentropic)
- 3 → 4: engine releases Q_C at constant temperature T_C (isothermal)
- 4 → 1: engine heats at constant entropy to T_H (isentropic)

Cycle returns engine to the same state so:

$$\oint dU = 0 = \oint \delta Q + \oint \delta W$$

\uparrow
 Integral
 around cycle

\uparrow
 These terms are not 0,
 there is net Q transferred
 and W done during cycle

\uparrow

We write δQ instead of dQ because they are not true differentials. Unlike U , which is a function of the state of the system only, Q and W will depend on the path of the integral.

Calculate $\oint \delta Q$:

$$\begin{aligned} \oint \delta Q &= \int_{1 \rightarrow 2} \delta Q + \int_{2 \rightarrow 3} \delta Q + \int_{3 \rightarrow 4} \delta Q + \int_{4 \rightarrow 1} \delta Q \\ &\quad \quad \quad Q_H \quad \quad 0 \quad \quad -Q_C \quad \quad 0 \\ &= T_H(S_2 - S_1) + T_C(S_4 - S_3) \\ &= T_H(S_2 - S_1) - T_C(S_2 - S_1) \end{aligned}$$

So, $\oint dU = 0 = (T_H - T_C)(S_2 - S_1) - \oint p dV$, and

$$W_{\text{engine}} = \oint p dV = (T_H - T_C)(S_2 - S_1) \quad \text{work done by the engine}$$

This is the area under the T-S curve for the Carnot cycle

$$\eta_c = \frac{W}{Q_H} = \frac{(T_H - T_C)(S_2 - S_1)}{T_H (S_2 - S_1)} = 1 - \frac{T_C}{T_H}$$

Although Carnot engine gives maximum efficiency η_c , it is not practical. Reversible cooling and heating processes with constant S are very slow.

Consider Carnot cycle realized with a monatomic ideal gas as a working substance:

Equation of state: $pV = Nk_B T$

Sackur-Tetrode equation: $S = Nk_B \left(\ln \frac{n_Q V}{N} + \frac{5}{2} \right)$

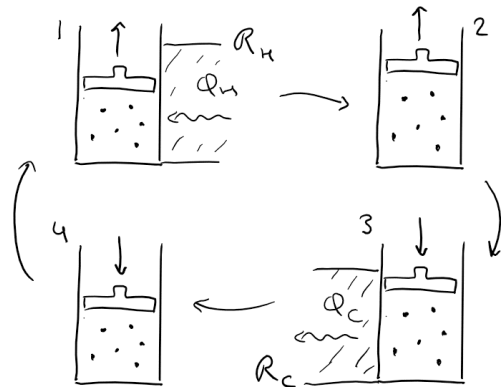
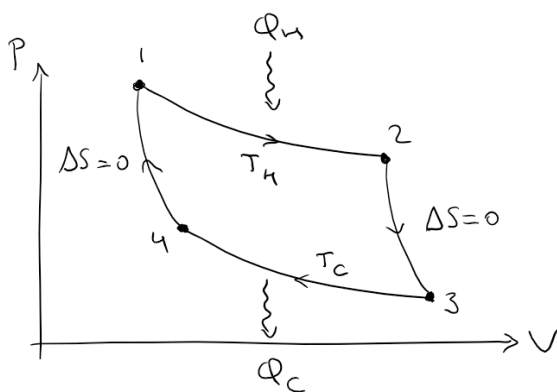
For isothermal segments of Carnot cycle ($1 \rightarrow 2, 3 \rightarrow 4$): $pV = \text{const.}$

For isentropic segments of cycle ($2 \rightarrow 3, 4 \rightarrow 1$): $S = \text{const.}$

$$S = Nk_B (\ln T^{3/2} + \ln V + \text{const.})$$

so $T^{3/2}V = \text{const.}$, and

$$(pV)^{3/2}V = p^{3/2}V^{5/2} = \text{const.} \quad \text{or} \quad pV^\gamma = \text{const.}, \quad \text{with } \gamma = \frac{5}{3}$$



$1 \rightarrow 2$: isothermal expansion at T_H : $pV = \text{const.}$

$2 \rightarrow 3$: isentropic expansion: $pV^\gamma = \text{const.}$

$3 \rightarrow 4$: isothermal compression at T_C : $pV = \text{const.}$

$4 \rightarrow 1$: isentropic compression: $pV^\gamma = \text{const.}$

Work done by engine = area enclosed in cycle = $+\oint pdV$:

$$\oint pdV = \underbrace{\int_{1 \rightarrow 2} pdV}_{W_{1 \rightarrow 2}} + \underbrace{\int_{2 \rightarrow 3} pdV}_{W_{2 \rightarrow 3}} + \underbrace{\int_{3 \rightarrow 4} pdV}_{-W_{3 \rightarrow 4}} + \underbrace{\int_{4 \rightarrow 1} pdV}_{-W_{4 \rightarrow 1}}$$

Each term represents the area under each part of the cycle. (Notice the negative signs. K & K define $W_{3 \rightarrow 4}$ and $W_{4 \rightarrow 1}$ in this way so that they are positive quantities.)

Question 2: Determine the work from 1 \rightarrow 2.

This is an expansion step at constant temperature T_H , so $pV = Nk_B T_H$ and:

$$W_{1 \rightarrow 2} = \int_{V_1}^{V_2} pdV = Nk_B T_H \int_{V_1}^{V_2} \frac{dV}{V} = Nk_B T_H \ln \frac{V_2}{V_1}$$

We could also have gotten this result from $W_{1 \rightarrow 2} = Q_H = T_H(S_2 - S_1)$ and using the Sackur-Tetrode equation, $S = Nk_B (\ln V + \text{const.})$:

$$W_{1 \rightarrow 2} = T_H(S_2 - S_1) = Nk_B T_H \ln \frac{V_2}{V_1}$$

The work done from 3 \rightarrow 4 is similarly:

$$W_{3 \rightarrow 4} = \int_{V_4}^{V_3} pdV = Nk_B T_C \int_{V_4}^{V_3} \frac{dV}{V} = Nk_B T_C \ln \frac{V_3}{V_4}$$

Question 3: Determine the work from 2 \rightarrow 3.

This is an expansion step at constant entropy. Using this and the thermodynamic identity,

$dU = TdS - pdV$, we can write

$$W_{2 \rightarrow 3} = \int_{U_2}^{U_3} dU = \frac{3}{2} Nk_B (T_H - T_C)$$

(It's tempting to use $pV^\gamma = \text{const.}$ but the value of const. is not obvious.)

The work done from 4 \rightarrow 1 is then:

$$W_{4 \rightarrow 1} = \int_{U_4}^{U_1} dU = \frac{3}{2} Nk_B (T_H - T_C) = W_{2 \rightarrow 3}$$

Now we simplify. During the isentropic expansion/compression, $T^{3/2}V = \text{const.}$, so:

$$T_H^{3/2}V_2 = T_C^{3/2}V_3 \quad \text{and} \quad T_C^{3/2}V_4 = T_H^{3/2}V_1$$

$$\text{so} \quad \frac{V_3}{V_2} = \left(\frac{T_H}{T_C}\right)^{3/2} = \frac{V_4}{V_1} \quad \text{or} \quad \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

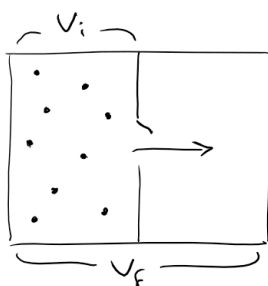
Putting it all together

$$\begin{aligned} W_{\text{engine}} &= W_{1 \rightarrow 2} + W_{2 \rightarrow 3} - W_{3 \rightarrow 4} - W_{4 \rightarrow 1} \\ &= Nk_B T_H \ln \frac{V_2}{V_1} + \cancel{\frac{3}{2} Nk_B (T_H - T_C)} - Nk_B T_C \ln \frac{V_3}{V_4} - \cancel{\frac{3}{2} Nk_B (T_H - T_C)} \\ &= Nk_B (T_H - T_C) \ln \frac{V_2}{V_1} = (T_H - T_C)(S_2 - S_1) \end{aligned}$$

the same answer, as expected.

EXTRA NOTE: Irreversible expansion

Imagine a closed system containing an ideal gas. The gas is allowed to expand into a vacuum:



No heat is transferred: $Q = 0$ (system is closed)

Energy is constant: $\Delta U = 0$ (U is independent of V for an ideal gas)

No work is done: $W = 0$

Temperature is constant: $\Delta T = 0$

Yet, entropy clearly increases: $\Delta S = Nk_B \ln \frac{V_f}{V_i} > 0$

This process is irreversible, because new entropy has been created and by 2nd law there is no way to remove it. The gas is not at equilibrium (i.e. in most probable configuration) at every moment of the expansion.

In reversible process of Carnot cycle, expansion moves a piston to extract work. The gas is at equilibrium at every moment of the expansion.

In general, for an irreversible process, we cannot say that $TdS = \delta Q$:

$$TdS > \delta Q_{\text{irrev}} \quad \text{and} \quad \delta W_{\text{irrev}} > dU - TdS$$

Compared to a reversible process:

$$TdS = \delta Q_{\text{rev}} \quad \text{and} \quad \delta W_{\text{rev}} = dU - TdS$$

so $\delta W_{\text{irrev}} > \delta W_{\text{rev}}$; excess work is done on the system to accomplish change. (In the example above, work done on gas during irreversible expansion is 0, work done on gas in reversible expansion is < 0).