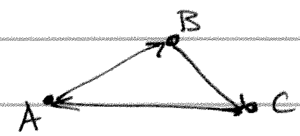
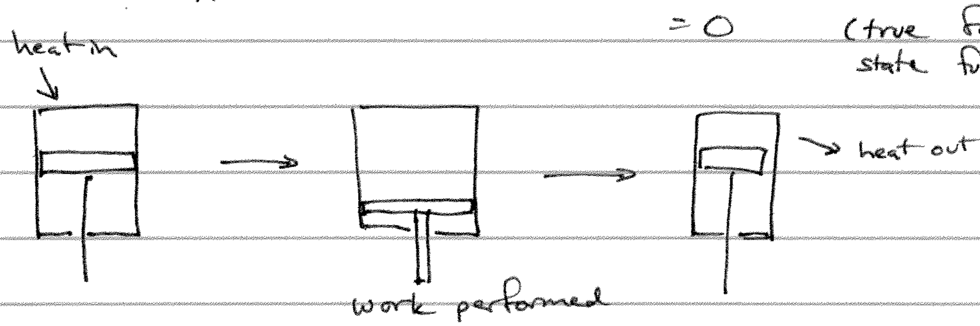
Thermodynamic cycles

A thermodynamic cycle is a set of processes that begin in one state, pass through other intermediate states, and then returns to the initial state



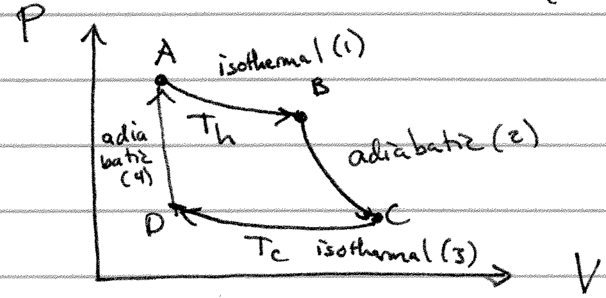
$$\Delta U = (U_B - U_A) + (U_C - U_B) + (U_A - U_C)$$
$$= 0$$ (true for all other state functions as well)



Thermodynamic cycles are the primary way we convert heat $\rightarrow$ work!

The Carnot Cycle

$P_A, V_A, T_A \longrightarrow P_C, V_C, T_C$ via two steps: an <u>isothermal</u> process & an <u>adiabatic</u> process (then 2 more to return home)



all of the steps are assumed to be reversible

$\Delta U = 0$ for the cycle, so $\delta q_{tot} = -\delta w_{tot}$

$$\delta q_{tot} = \delta q_{(1)} + \cancelto{0}{\delta q_{(2)}} + \delta q_{(3)} + \cancelto{=0\ \text{(adiabatic)}}{\delta q_{(4)}}$$

For an isothermal process, $\delta q = NkT \ln\left(\frac{V_2}{V_1}\right)$

$$\delta q_{tot} = NkT_h \ln\left(\frac{V_B}{V_A}\right) + NkT_c \ln\left(\frac{V_D}{V_C}\right)$$

For an adiabatic process, we derived $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{Nk/C}$

So in the Carnot cycle

$$\frac{V_C}{V_B} = \left(\frac{T_h}{T_c}\right)^{C_v/Nk} \quad \text{and} \quad \frac{V_D}{V_A} = \left(\frac{T_h}{T_c}\right)^{C_v/Nk}$$

$$\therefore \quad \frac{V_C}{V_B} = \frac{V_D}{V_A} \quad \Longrightarrow \quad \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

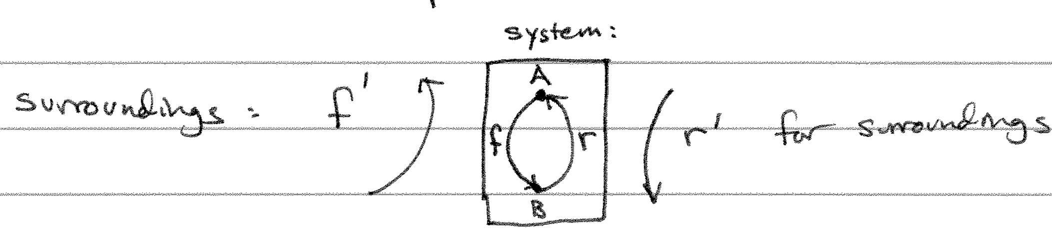
So:

$$\delta \omega_{tot} = -\delta q_{tot} = -NkT_h \ln\left(\frac{V_B}{V_A}\right) + NkT_c \ln\left(\frac{V_B}{V_A}\right)$$

$$= -Nk(T_h - T_c)\ln\left(\frac{V_B}{V_A}\right)$$

The work performed by a Carnot engine depends on the difference between intake & exhaust temperatures and the compression ratio: V_B / V_A

Efficiency : The maximum possible work we can do is achieved via a reversible process.



For the <u>system</u> itself: $\Delta S = \Delta S_f + \Delta S_r = 0$
state function

The 2^{nd} law states: $\Delta S_f + \Delta S_{f'} \geq 0$

$\Delta S_r + \Delta S_{r'} \geq 0$

The <u>total</u> entropy change for <u>system</u> + <u>surroundings</u> ≥ 0 for each leg of the process.

The only time we get the <u>equality</u> is if we're at equilibrium. If we invoke reversibility for all legs then the system <u>and</u> surroundings must return back to their original states, and $\Delta S = \Delta S_f + \Delta S_r + \Delta S_{f'} + \Delta S_{r'} =$

This also implies $\Delta S_{f'} + \Delta S_{r'} = 0$ for a reversible cyclic process.

ΔS for a <u>Carnot cycle</u>

$$\Delta S = \Delta S_{AB} + \Delta S_{BC} + \Delta S_{CD} + \Delta S_{DA}$$

adiabatic, so $\Delta S = \frac{q}{T} = 0$

$$\Delta S = \Delta S_{AB} + \Delta S_{CD}$$

For a <u>reversible</u> isothermal process $\Delta S = \frac{\delta q}{T} = Nk\ln\left(\frac{V_2}{V_1}\right)$

so:

$$\Delta S_{AB} = Nk\ln\left(\frac{V_B}{V_A}\right)$$

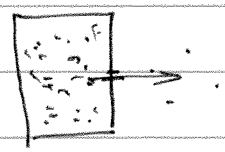
$$\Delta S_{CD} = Nk\ln\left(\frac{V_D}{V_C}\right) = N\ln\ln\left(\frac{V_A}{V_B}\right)$$

So: $\Delta S = \Delta S_{AB} + \Delta S_{CD} = 0$

$\therefore$ the Carnot cycle is reversible (which we kind of expect since each step was specified to be reversible)

Now let's consider an irreversible process

Free expansion is irreversible:



$P_{ext} = 0$

$\delta w = -P_{ext}\, dV = 0$ for a free expansion into a vaccuum

If the free expansion is also done adiabatically then $\delta q = 0$ and $\Delta U = \delta w + \delta q = 0$

Since: $\Delta U = C_v \Delta T \implies \Delta T = 0$

To find ΔS_{system} let's assume temporarily that the process is reversible (even though it isn't)

Since S is a state function, this is ok, the path we take doesn't matter:

$$\Delta S_{system} = Nk \ln\left(\frac{V_2}{V_1}\right) > 0 \quad \text{because } V_2 > V_1$$

$$\Delta S_{surroundings} = \frac{q_{rev}}{T} = 0 \quad \text{because we're adiabatic}$$

$$\therefore \quad \Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

$\therefore$ The expansion of the gas leads to a total increase in entropy and is therefore irreversible

Some other irreversible processes:

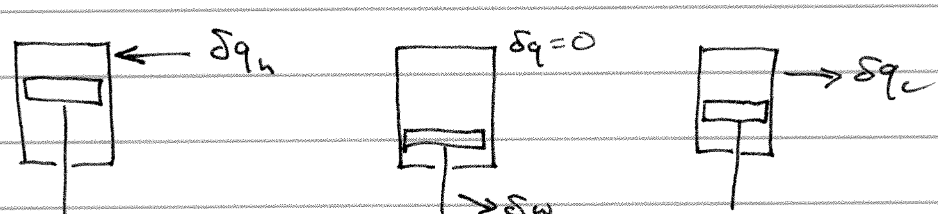
- Diffusion & mixing: $\Delta S_{system} > 0$ when molecules mix even when there is no change in the surroundings $\therefore$ $\Delta S_{total} > 0$

- Heat flows from a hot object to a cold object. Again $\Delta S_{system} > 0$ even when there is no changes in surroundings $\therefore$ $\Delta S_{total} > 0$

- Friction — A gas expanding through a piston can move a weight through some distance, but if there is friction, the distance will be smaller, so less <u>work</u> will be performed, heating the surroundings and leading to $\Delta S_{total} > 0$

- Others: Boiling an egg, fluid flow, etc.

Why do engines waste heat?



$\Delta U = 0 \quad \therefore \quad \delta q = \delta q_h - \delta q_c$

$$\text{efficiency} = \eta = \frac{\delta w}{\delta q_h} = 1 - \frac{\delta q_c}{\delta q_h}$$

← work output

← heat input

Now let's figure out the efficiency for a Carnot cycle:

$$\Delta S = \Delta S_h + \Delta S_c + \underset{\substack{\parallel \\ 0}}{\Delta S_w}$$

because the work is performed adiabatically

In a reversible cycle, $\Delta S = \Delta S_h + \Delta S_c$

$$\Delta S_h = \frac{\delta q_h}{T_h} \qquad \Delta S_c = \frac{-\delta q_c}{T_c}$$

$\therefore$

$$\frac{\delta q_c}{\delta q_h} = \frac{T_c}{T_h}$$

The <u>maximum</u> efficiency $\eta = 1 - \frac{T_c}{T_h}$

Since $T_c < T_h$ in a realistic engine there's an inherent inefficiency

When $T_c = 0$, we reach a point where heat can be converted to work with 100% efficiency. This is also how we define the absolute 0 of temperature!