Lecture 17 Heat + Work

Recall thermodynamic identity:

$$dU = \underbrace{T\,dS}_{\text{heat}} \underbrace{- p\,dV}_{\text{work}}$$

2 ways to transfer energy between systems

Heat: $đQ \equiv T\,dS$

Work: $đW \equiv -p\,dV$ (here, specifically mechanical work)

(We'll explain what đ symbol means later)

$\therefore \quad dU = đQ + đW$

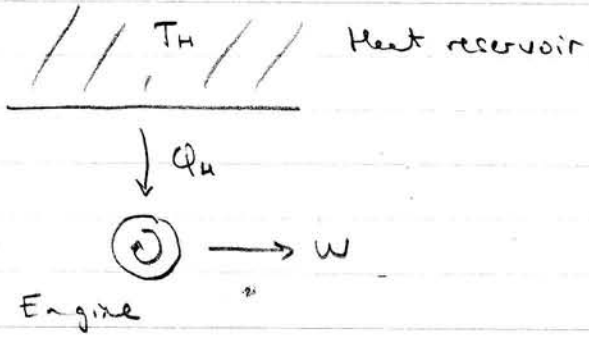
1st law of thermodynamics (conservation of energy)

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

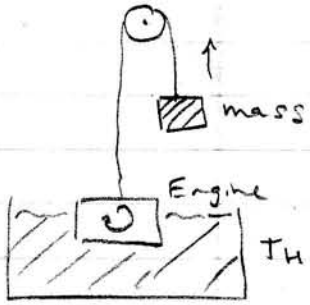
1) Work – all types of work can be interconverted. For example, an ideal electrical motor can convert electrical work entirely into mechanical work

2) 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

Let's see why. 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. $dU = 0$



Ex: Engine lifts mass



During each cycle heat Q_H goes in, Work W done, returns engine to same state so $U_{before} = U_{after}$

By 1st law: $Q_H = W$

What about entropy? Consider the total isolated system (reservoir + engine + mass):

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

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

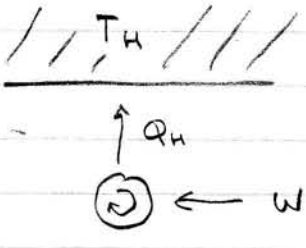
Engine returns to same state so $\Delta S_{engine} = 0$

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

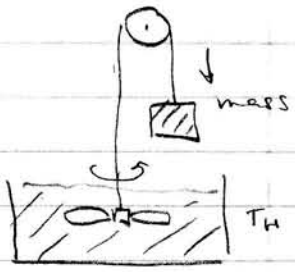
$\therefore \Delta S_{tot} = \Delta S_{res} < 0$ violates 2nd law!

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

Notice the reverse process is fine:

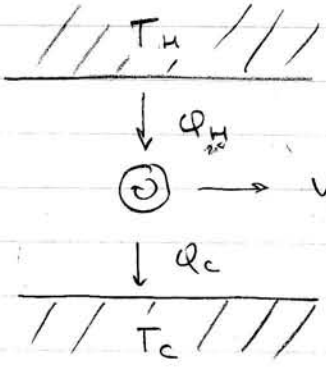


Ex: mass rotates propeller



Here $\Delta S_{tot} > 0$

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



1st law: $Q_H = Q_C + W$

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

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

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 $\eta = \frac{W}{Q_H}$ How much of the heat can be converted to work?

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

The best we can do is put back all entropy lost into C reservoir
so $\Delta S_{tot} = -\frac{Q_H}{T_H} + \frac{Q_C}{T_C} = 0$

$\therefore \frac{Q_C}{Q_H} = \frac{T_C}{T_H}$ and $\boxed{\eta_C = 1 - \frac{T_C}{T_H}}$ Carnot efficiency

This is the highest possible efficiency for a heat engine
Ex: in power plant steam turbines $T_H \approx 600K$, $T_C \approx 300K$
so $\eta_C = 50\%$ (in practice 40%)

$\eta_C \to 1$ only when $T_C/T_H \to 0$

In practice $\Delta S > 0$ because additional entropy is created during cycle:

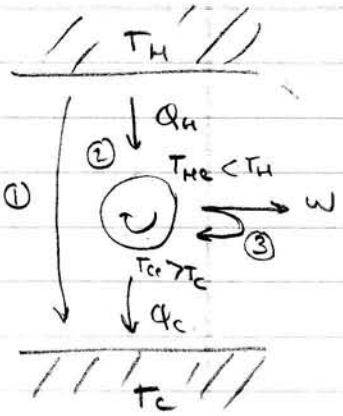
$$\Delta S_{H,rs} = -\frac{Q_H}{T_H} \qquad \Delta S_{C,rs} = \frac{Q_C}{T_C} + \Delta S_{irr}$$

$$\Rightarrow \quad \eta = 1 - \frac{T_C}{T_H} - T_C \frac{\Delta S_{irr}}{Q_H} < \eta_C$$

This process is irreversible - once entropy is created, can't be removed

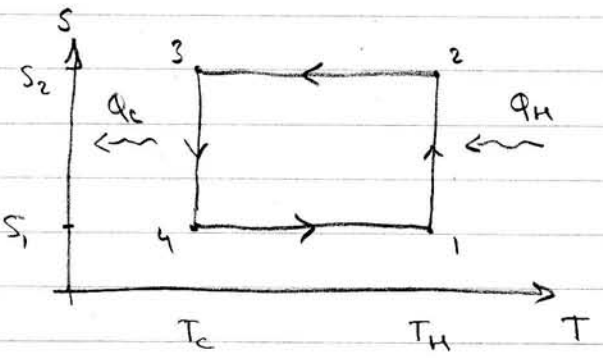
Ex sources of irreversibility

1) Heat bypass - heat transfered 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 - we'll discuss this soon.



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

The Carnot cycle (assume no irreversibility)



1 → 2 : engine takes in Q_H at T_H

2 → 3 : engine cools at constant entropy to T_C

3 → 4 : engine releases Q_C at T_C

4 → 1 : engine heats at constant entropy to T_H

$1 \to 2$ and $3 \to 4$ are constant T = isothermal
$2 \to 3$ and $4 \to 1$ are constant S = isentropic

Cycle returns engine to same state so:

$$\oint dU = 0 = \underbrace{\oint đQ - \oint p\,dV}$$

↑ integral around cycle

these are not = 0
there is a net heat transfer + net work done during cycle*

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

Calculate $\oint đQ = \underbrace{\int_{1\to2} đQ}_{Q_H} + \underbrace{\int_{2\to3} đQ}_{0} + \underbrace{\int_{3\to4} đQ}_{-Q_C} + \underbrace{\int_{4\to1} đQ}_{0}$

$Q_H = T_H(S_2 - S_1)$

$-Q_C = T_C(S_4 - S_3) = -T_C(S_2 - S_1)$

$$\therefore \oint dU = 0 = T_H(S_2 - S_1) + T_C(S_4 - S_3) - W_{engine}$$

$$\eta = \frac{W}{Q_H} = \frac{W}{T_H(S_2 - S_1)} = 1 + \frac{T_C(S_4 - S_3)}{T_H(S_2 - S_1)} = 1 - \frac{T_C}{T_H} = \eta_C \quad \checkmark$$

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

Although Carnot engine gives maximum efficient η_C it is not practical. Reversible cooling + heating processes with constant S are very slow

Consider Carnot cycle realized with an ideal gas
Visualize cycle in p-V plot

Recall equation of state $pV = Nk_BT$
and Sackur-Tetrode eq'n: $S = Nk_B\left[\ln\left(\frac{n_Q}{n}\right) + \frac{5}{2}\right]$

So for isothermal parts of cycle $1 \to 2$, $3 \to 4$:
$\therefore$ $\boxed{pV = \text{const.}}$

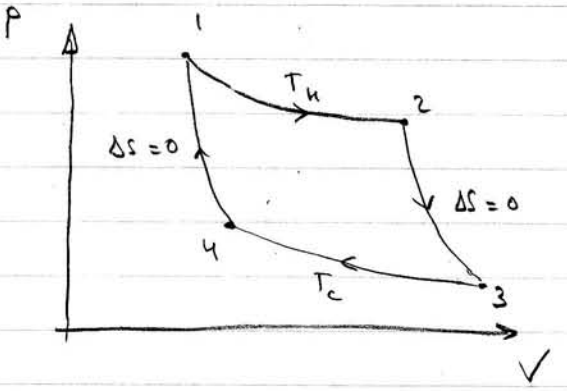
For isentropic parts of cycle $2 \to 3$, $4 \to 1$:

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

$\therefore$ $T^{3/2}V = \text{const.}$ ← since $n_Q \propto T^{3/2}$ $n \propto \frac{1}{V}$

$$(pV)^{3/2}V = p^{3/2}V^{5/2} = \text{const}$$

$\therefore$ $\boxed{pV^\gamma = \text{const.}}$ $\qquad \gamma = \frac{5}{3}$



$1 \to 2$: isothermal expansion at T_H
$pV = \text{const.}$
$2 \to 3$: isentropic expansion
$pV^\gamma = \text{const.}$
$3 \to 4$: isothermal compression at T_C
$pV = \text{const.}$
$4 \to 1$: isentropic compression.
$pV^\gamma = \text{const.}$

$\oint p\,dV$ = area enclosed in cycle = work done by system

$$= \int_{1\to2} + \int_{2\to3} + \int_{3\to4} + \int_{4\to1} p\,dV$$

$$= W_{12} + W_{23} - W_{34} - W_{41}$$

= areas under each part of cycle

$$W_{12} = \int_{V_1}^{V_2} p\,dV = N k_B T_H \int_{V_1}^{V_2} \frac{dV}{V} = N k_B T_H \ln \frac{V_2}{V_1}$$

(could also get this from $W_{12} = Q_H = T_H (S_2 - S_1) = N k_B T_H \ln \frac{V_2}{V_1}$)

$$\therefore W_{34} = N k_B T_C \int_{V_4}^{V_3} \frac{dV}{V} = N k_B T_C \ln \frac{V_3}{V_4}$$

For W_{23}, W_{41} use fact that $\Delta S = 0$ so

$$W_{23} = U(T_H) - U(T_C) = \tfrac{3}{2} N k_B (T_H - T_C)$$
$$W_{41} = U(T_H) - U(T_C) = W_{23}$$ they cancel out

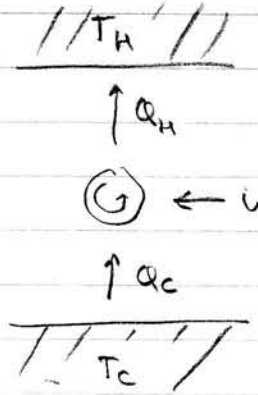
Now simplify: During isentropic expansion/compression:

$$T_H^{3/2} V_2 = T_C^{3/2} V_3 \qquad T_C^{3/2} V_4 = T_H^{3/2} V_1$$

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

$$\therefore W = N k_B (T_H - T_C) \ln \frac{V_2}{V_1} = N k_B (T_H - T_C)(S_2 - S_1) \quad \checkmark$$

Refrigerators are heat engines run in reverse



Move Q_C from cold place to a warm place

By 1st law: $Q_C + W = Q_H$

By 2nd law:

$$-\frac{Q_C}{T_C} + \frac{Q_H}{T_H} \geq 0 \quad \text{or} \quad \frac{Q_H}{Q_C} \geq \frac{T_H}{T_C}$$

Generally care about how much heat can be extracted for given W

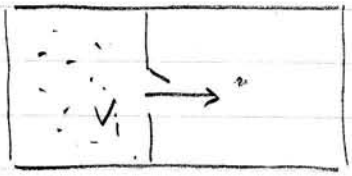
γ = coefficient of performance $= \frac{Q_C}{W}$

$$\gamma = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C} = \frac{1}{Q_H/Q_C - 1} \leq \frac{1}{T_H/T_C - 1} = \frac{T_C}{T_H - T_C} = \gamma_C$$

↑ Carnot coefficient

Irreversibility

Consider a gas suddenly expanding into a vacuum



The total system is isolated
There is no change in energy
(U is independent of V for ideal gas)
so $dU = 0$.

No heat transfered so $q = 0$, and no change in temperature so $dT = 0$. Yet entropy clearly increases:

$$\Delta S = S_2 - S_1 = N k_B \ln \frac{V_2}{V_1} > 0$$

So we cannot say $dS = \frac{dq}{T}$ for irreversible process

$$T dS > dq_{irr} \quad \text{and from 1st law} \quad dw_{irr} > dU - T dS$$

Process is irreversible because new entropy is created, and by 2nd law there is no way to destroy it.

Compare to a reversible process $dq_{rev} = T dS$, $dw_{rev} = dU - T dS$

$\therefore \quad dw_{irr} > dw_{rev} \qquad dq_{irr} < dq_{rev}$