

Thermal Physics

I Last time

II Review of 2nd law

logic.

III Real Heat Engines

IV Refrigerators

Meeting XII

Free expansion

$$T_2 = T_1$$

ideal gas

$$T_2 < T_1$$

van der Waals gas

Comes from cons. of energy.

Throttling Enthalpy conserved

$$H(T_2, P_2) = H(T_1, P_1)$$

Lead to consideration of

$$\mu \equiv \left(\frac{\partial T}{\partial P}\right)_H$$

the "Joule-Thompson" coeff.

$\mu > 0 \rightarrow$ cooling of gas

Heat Engines

Perfect engine is impossible



perfect if



$$Q = W$$

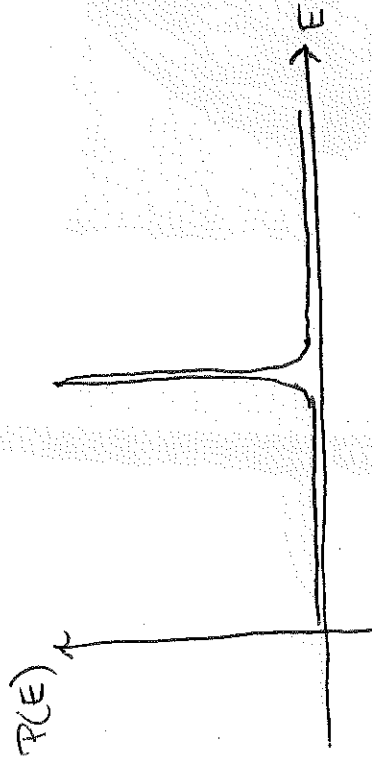


Not possible!

II Review of 2nd Law

logic

Recall



because of the huge # of d.o.f.

But then when

$$A, T_i$$

$$A', T_i'$$

$$P(E) = C \Omega(E) \Omega(E')$$

with $E' = E^{(0)} - E$, then

$$\ln P(E) = \ln C + \ln \Omega + \ln \Omega'$$

and we learn

$$S_f + S_f' \geq S_i + S_i'$$

When does equality hold?

are put into thermal contact $P \propto 1/S$
 they are in very low probability
 state \rightarrow the system evolves
 toward higher probability,
 which is achieved when

$$P_f = P_f' \text{ or } T_f = T_f'$$

The final probability is maximum
 and hence can't be less than
 the initial one!

$$\Delta S_{\text{tot}} = \Delta S + \Delta S' \geq 0 \quad \text{2nd law.}$$

\rightarrow If the two systems are
 already in equilibrium then
 certainly $\Delta S_{\text{tot}} = 0$ (already
 at prob. max.) More generally
 if they are infinitesimally
 separated \downarrow adiabatic

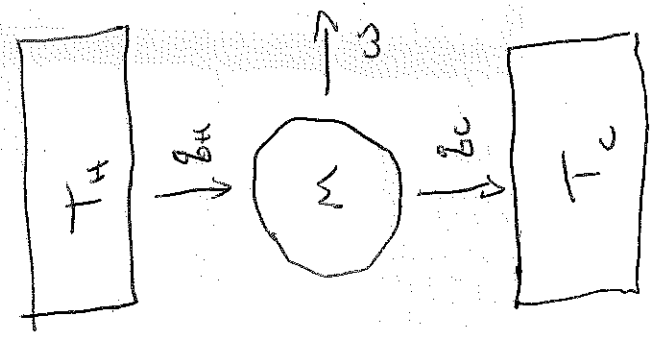
$$dS = \frac{\delta Q}{T} = 0 \Rightarrow \Delta S = 0$$

for quasi-static.

Our proof that there was no perfect engine was just the 2nd law. Hence it is a form of the 2nd law

It is impossible to construct a perfect heat engine.

Kelvin's formulation of 2nd law



and now the 2nd law gives

$$\Delta S = -\frac{Q_H}{T_H} + \frac{Q_C}{T_C} \geq 0$$

Putting these together

$$-\frac{Q_H}{T_H} + \frac{Q_H - W}{T_C} \geq 0$$

III Instead of trying to extract energy from random motion and turn it purely into work we can do some work and cause some random motion. Conservation of energy is

$$Q_H = W + Q_C$$

$$\Rightarrow \frac{W}{T_C} \leq Q_H \left(\frac{1}{T_C} - \frac{1}{T_H} \right)$$

Introduce "efficiency"

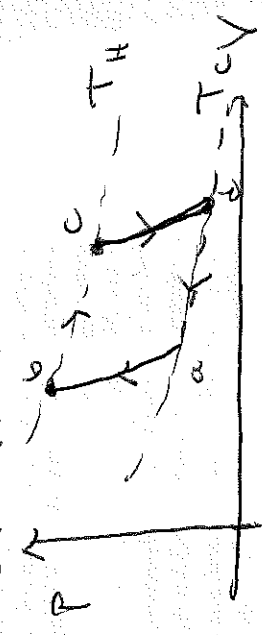
$$\eta = \frac{W}{Q_H}$$

then

$$\eta = \frac{W}{Q_H} \leq 1 - \frac{T_C}{T_H} = \frac{T_H - T_C}{T_H}$$

What engine realizes this maximum efficiency?

A Carnot engine, which consists of two adiabats and two isotherms



Similarly, $q_c = \nu R T_c \ln\left(\frac{V_d}{V_a}\right)$

Then
$$\eta = \frac{w}{q_H} = \frac{q_H - q_c}{q_H} = 1 - \frac{\nu R T_c \ln\left(\frac{V_d}{V_a}\right)}{\nu R T_H \ln\left(\frac{V_c}{V_b}\right)} = 1 - \frac{T_c}{T_H} \frac{\ln\left(\frac{V_d}{V_a}\right)}{\ln\left(\frac{V_c}{V_b}\right)}$$

How to find Vol ratios?

For a perfect engine $\eta = \frac{w}{q_H} = 1$ (not possible)

in reality $\eta = \frac{q_H - q_c}{q_H} < 1$

Best we can do is a quasi-static engine with $\eta = \frac{T_H - T_C}{T_H}$

Ideal gas: $PV = \nu RT$
and $PV^\gamma = \text{const.}$ adiabat
~~heat~~ $dE = \delta Q - dW$ along isotherms

$b \rightarrow c$ isotherm $\Rightarrow dE = 0$ so $\delta Q = dW$
or $q_H = \int_{V_b}^{V_c} P dV = \int_{V_b}^{V_c} \frac{\nu R T_H}{V} dV = \nu R T_H \ln\left(\frac{V_c}{V_b}\right)$

We did this together. Use the fact that $a \rightarrow b$ and $c \rightarrow d$ are adiabats while $b \rightarrow c$ and $d \rightarrow a$ are isotherms to prove

$$\frac{V_d}{V_a} = \frac{V_c}{V_b}$$

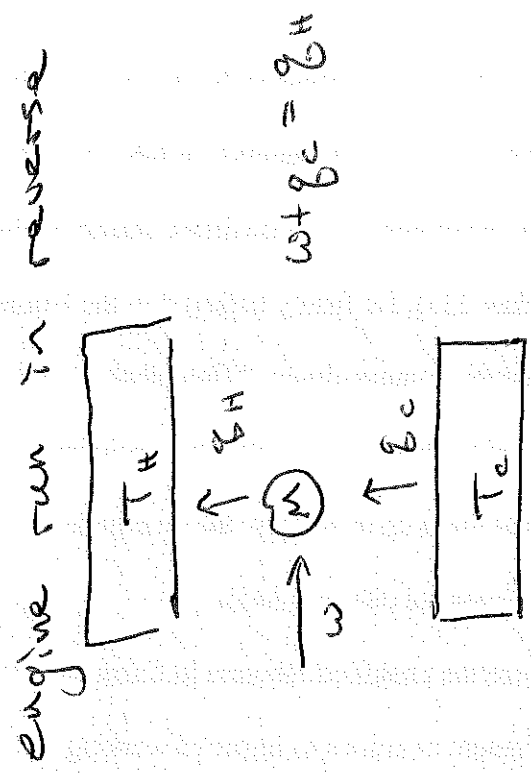
and hence $\boxed{\eta = 1 - \frac{T_c}{T_H}}$

Again from the 2nd law a Perfect refrigerator, with $q_c = q_H$ and $w = 0$ is impossible.

For a real refrigerator we again characterize its performance by

$$\gamma \equiv \frac{\text{what we want}}{\text{what we pay}} = \frac{q_c}{w}$$

PS/5
IV A refrigerator is essentially a heat engine run in reverse



This is

$$\gamma = \frac{q_c}{q_H - q_c}$$

By the 2nd law

$$\Delta S = \frac{q_H}{T_H} + \frac{(-q_c)}{T_c} \geq 0$$

$$\Rightarrow \frac{q_c}{q_H} \leq \frac{T_c}{T_H}$$

and so at best

$$\boxed{\gamma = \frac{1}{\frac{T_H}{T_c} - 1} = \frac{T_c}{T_H - T_c}}$$

cannot for refrigerator