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Lecture 3 - Ideal Gas + Balances

Ideal gas

What is it? Particles with mass, no volume, interact by purely elastic collisions.

Empirically have:

- i) $PV = N k_B T = n RT$ R: gas const.
- ii) U only depends on T
particles don't interact

In simple case, appropriate to monatomic gases and to polyatomics over restricted T ranges, have

$$U = c N k_B T \quad c = \begin{cases} \frac{3}{2} & \text{monatomic} \\ \frac{5}{2} & \text{diatomic (rot)} \end{cases}$$

U as a variable suggests entropy representation

$$\frac{1}{T} = c \frac{N R}{U} = \frac{c R}{U} \quad \frac{P}{T} = \frac{N R}{V} = \frac{R}{v}$$

$$dS = \frac{c R}{U} dU + \frac{R}{v} dv \rightarrow$$

$$S(U, v) = c R \ln\left(\frac{U}{U^\circ}\right) + R \ln\left(\frac{v}{v^\circ}\right) + S_0, \quad S_0 = S(U^\circ, v^\circ)$$

- or

$$S(U, v, N) = N \left[R \ln \left[\left(\frac{U}{U^\circ} \right)^c \left(\frac{v}{v^\circ} \right) \left(\frac{N}{N^\circ} \right)^{(c+1)} \right] + S_0 \right]$$

Might be more intuitive to express in terms of T

$$S(T, v, N) = c N R \ln \frac{T}{T^\circ} + N R \ln \frac{v}{v^\circ} + N S_0$$

Could get μ by differentiation or by Gibbs-Duhem

(2)

~~Using stat. mech., can show that~~

$$S_0 = \frac{3}{2} k \left(\frac{5}{3} + \ln \frac{4\pi m}{3h^3} \right)$$

~~where m is the molecular mass and h Planck's constant.~~

Sackur-Tetrode eqn

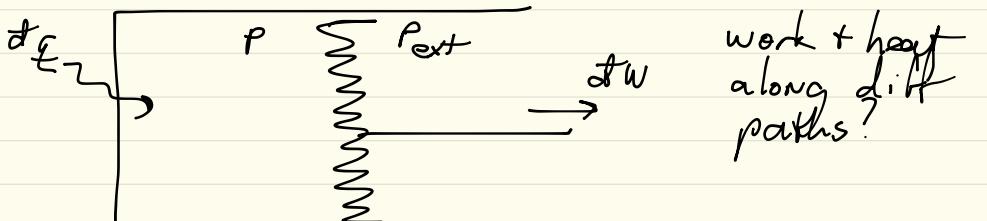
$$S(T, V, N) = cNR \ln \frac{T}{T_0} + NR \ln \frac{V}{Nv_0} + Ns_0$$

momentum DOFs position DOFs

$S = k \ln \Omega$. What are the "microstates" to count in an ideal gas?
 Each molecule specified by $\{\vec{r}, \vec{p}\}$ pair, position (scals w/V) and momentums (scals w/T)

The two EOS's above could have been inferred from gas kinetic theory + the Boltzmann distribution, and S from stat. mech.

Let's put the fundamental eq to work



$$\begin{aligned} dU &= TdS - Pdv \\ &= dQ^{\text{qs}} + dW^{\text{qs}} \end{aligned}$$

adiabatic QS work

① start from fund eq...

$$TdS = 0 \leftrightarrow dQ_{\text{gas}} = 0$$

$$s(u, v) = cR \ln\left(\frac{u}{u_0}\right) + R \ln\left(\frac{v}{v_0}\right)$$

$$W = \Delta U \quad u^c v = \text{const} \quad u = u_0 \left(\frac{v_0}{v}\right)^{1/c}$$

$$u - u_0 = \left[\left(\frac{v_0}{v}\right)^{1/c} - 1 \right] u_0$$

$T \downarrow$

$$\left[\left(\frac{v_0}{v}\right)^{1/c} - 1 \right] \cdot cRT_0$$

$$= c R (T - T_0)$$

reversible? Yes!

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Alt approach: integrate $-PdV$

$$W = - \int P_{ad} dV \quad \text{what's } P_{ad}(V) \text{?} \quad \begin{matrix} \text{integrate} \\ P \propto V \end{matrix}$$

adiabat $s \text{ const} \rightarrow u^\gamma v = \text{const}$

$$u = cRT = cPV \rightarrow P^c V^{c+1} = \text{const}$$

$$P V^{\frac{c+1}{c}} = \text{const}$$

$$\gamma = \frac{c+1}{c}$$

$$P = P_0 \left(\frac{V_0}{V} \right)^\gamma \quad \underline{\text{adiabat}}$$

$$W = - \int P_0 \left(\frac{V_0}{V} \right)^\gamma dV = \dots - \frac{RT_0}{1-\gamma} \left[\left(\frac{V}{V_0} \right)^{1-\gamma} - 1 \right]$$

same answer!

$$1 - \gamma = -\frac{1}{c}$$

(3) Another alt approach, starting f. EOS.

$$S = \text{const} \rightarrow dS = 0 \rightarrow dU = dW_{ad} = -PdV$$

cos cos

$$U = c RT = c PV \rightarrow dU = c(PdV + VdP)$$

$$-PdU = c(PdV + VdP) \rightarrow$$

or just set $S \infty$
to + const.

$$(c+1) \frac{dU}{V} = -c \frac{dP}{P} \rightarrow P^c V^{c+1} = \text{const}$$

$$P V^\gamma = \text{const} \quad \text{adiabat}$$

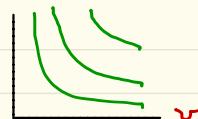
$$W_{ad} = - \int PdV \xrightarrow{\text{some work}} - \frac{RT_0}{1-\gamma} \left[\left(\frac{V}{V_0} \right)^{1-\gamma} - 1 \right]$$

$\hookrightarrow -P_0 V_0^\gamma \int V^{-\gamma} dV \quad \uparrow$

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Fun with an ideal gas
isothermal expansion

^{not}
physical



$$T = \text{const} \rightarrow U = \text{const} \rightarrow PV = \text{constant} \quad (\text{NRT})$$

isotherms

$$\delta Q = -\delta W$$

$$S(u, v) = cR \ln\left(\frac{u}{u_0}\right) + R \ln\left(\frac{v}{v_0}\right)$$

$$\Delta S_{\text{sys}} = S_f - S_i = NR \ln\left(\frac{V}{V_0}\right)$$

entropy of system increases

$$Q_{\text{qs}} = T \Delta S = RT \ln\left(\frac{V}{V_0}\right)$$

$$\Delta U = 0 \rightarrow Q_{\text{qs}} = -W_{\text{qs}} = RT \ln\left(\frac{V}{V_0}\right)$$

heat flows to compensate work

- OR -

$$W_{\text{qs}} = - \int P dV = -RT \int \frac{dV}{V}$$

$$W_{\text{qs}} = -RT \ln\left(\frac{V}{V_0}\right)$$

expansion extracts work

reversible? YES!

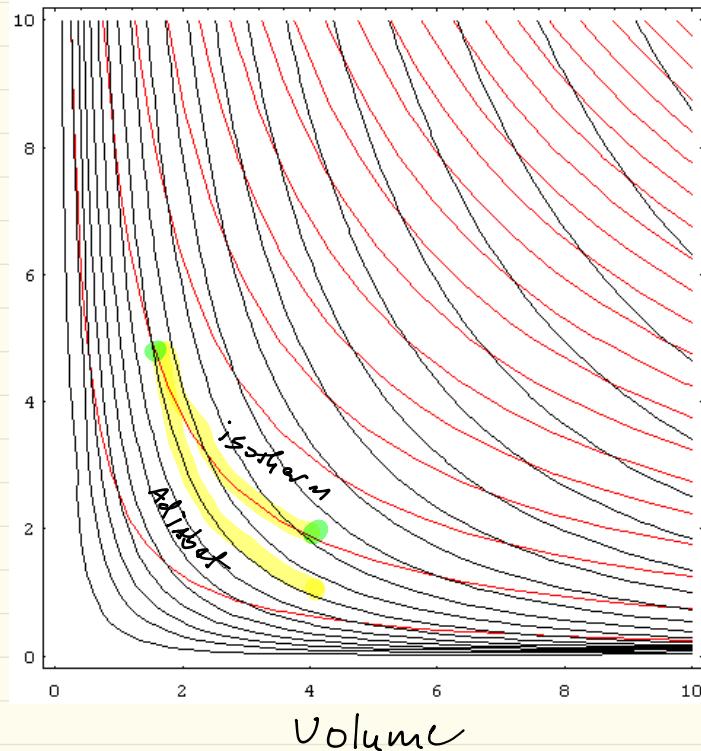
$$\Delta S_{\text{sur}} = Q_{\text{sur}}/T = -Q_{\text{qs}}/T$$

$$= -\Delta S_{\text{sys}}$$

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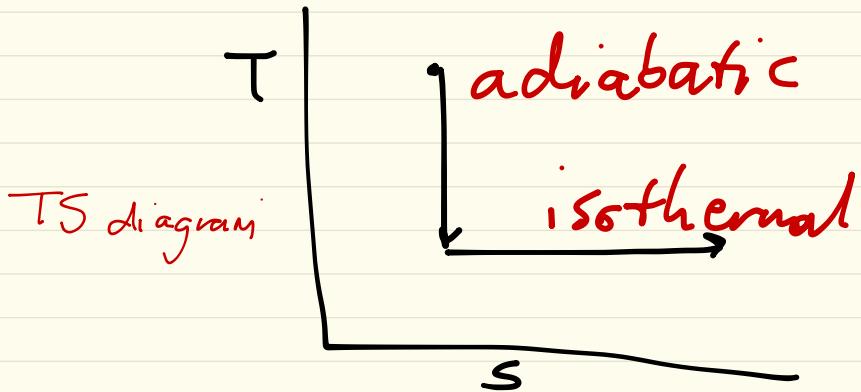
$$\left(\frac{\partial P_{ad}}{\partial V}\right) > \left(\frac{\partial P_{iso}}{\partial V}\right)$$

Pressure



red: isotherms

black: adiabats



Who does more work? adiabatic or isothermal?

$$V = 2V_0 \quad T_0 = 500 \text{ K} \quad N = 1 \quad c = \frac{3}{2} \rightarrow \gamma = \frac{5}{3}$$

$$W_{\text{iso}} = -500R \ln 2 \quad W_{\text{Ad}} = -500R (0.56) \\ -500R (0.69)$$

winner!

$$\Delta U_{\text{Ad}} = W_{\text{Ad}} = -\frac{NRT_0}{1-\gamma} \left[\left(\frac{V}{V_0} \right)^{1-\gamma} - 1 \right] = cNR(T-T_0)$$

$$\Rightarrow T = T_0 \cdot \left(\frac{1}{2} \right)^{\frac{1}{\gamma-1}} = 315 \text{ K} \quad T \text{ decreases}$$

$$\text{Can use this to show } \frac{T}{T_0} = \left(\frac{P}{P_0} \right)^{\frac{\gamma-1}{\gamma}}$$

$$P_{\text{ad}} = P_0 \left(\frac{1}{2} \right)^{5/3} \quad P_{\text{iso}} = P_0 \cdot \left(\frac{1}{2} \right)$$

No entropy change anywhere!

Example

Adiabatic free expansion

$$\delta W = 0 \quad \delta q = 0 \quad \Delta U = 0 \quad \Delta T = 0$$

$$\text{From fundamental eq} \quad \Delta S = N R \ln \frac{V}{V_0}$$

Exactly the same as isothermal, because end states the same. But, $\delta q = 0 \rightarrow \Delta S_{\text{sur}} = 0$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} > 0 ! \quad \text{irreversible}$$

(8)

Isothermal process + free expansion
 both start and end at the same place, but different w & q . What's the max w one can get?

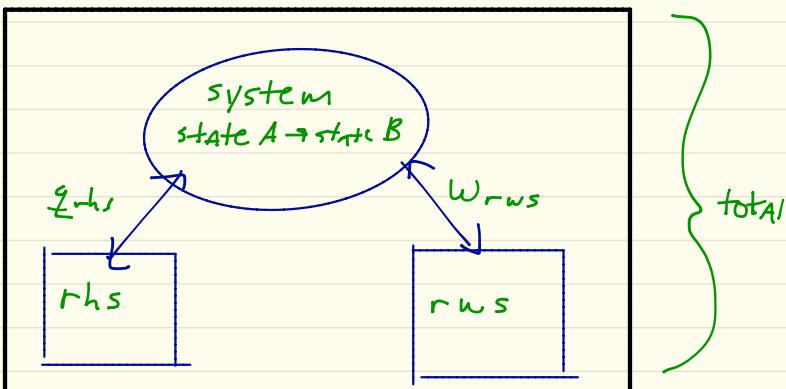
reversible work source - reservoir to which we can add or remove work reversibly. All processes w/i RHS are quasi-static and isentropic

reversible heat source - reservoir to which we can add or remove heat reversibly. All processes w/i RHS are quasi-static

RHS characterized by a heat capacity $C(T)$

$$dU_{rhs} = \cancel{dq}_{rhs} = C(T) dT$$

$$dS_{rhs} = \cancel{dq}_{rhs}/T = \frac{C(T)}{T} dT$$



What's the maximum work that can be done in taking the system from some state A to some other state B?

$$U(S^A, V^A, N_1^A, N_2^A, \dots) \rightarrow U(S^B, V^B, N_1^B, N_2^B, \dots)$$

one step, several, reversible, irreversible?

maximum work theorem:

The delivery of work is maximum and heat is minimum for an overall reversible process ($dS_{tot} = 0$). The work + heat are identical for every reversible process.

Consider infinitesimal change $A \rightarrow B$, so system energy change is dU .

Let $dW_{rhs} > 0$ for work done by system
 $dq_{rhs} > 0$ " heat taken from system

Energy conservation $\rightarrow dU + dq_{rhs} + dW_{rhs} = 0$

Entropy maximum $\rightarrow dS_{tot} = dS + dS_{rhs}$
 $= dS + dq_{rhs}/T_{rhs} \geq 0$

$$dq_{rhs} \geq -T_{rhs} dS$$

$$\begin{aligned} dW_{rhs} &= -(dU + dq_{rhs}) \\ &\leq -(dU - T_{rhs} dS) \end{aligned}$$

$$dW_{rhs} \leq T_{rhs} dS - dU$$

T_{rhs} , ΔU , ΔS are all specified, so right hand side is specified. ΔS is limit.

How to maximize ΔW_{rhs} ? Minimize ΔQ_{rhs} .
 Minimum is $\Delta Q_{rhs} = -T_{rhs} \Delta S \rightarrow \boxed{\Delta S_{tot} = 0}$

Perhaps not surprising, but process that creates the most useful work is the one that overall creates no entropy. By construction, all such processes have same $Q + W$.

In finite difference form, have

$\Delta S, \Delta U$
apply to system

energy cons: $\Delta U + Q_{rhs} + W_{rhs} = 0$

reversible: $\Delta S_{tot} = \Delta S + \int \frac{dQ_{rhs}}{T_{rhs}} = 0$

If we know $C_{rhs}(T) = \frac{dQ_{rhs}}{dT}$, then

$$\Delta S_{tot} = \Delta S + \int \frac{C_{rhs}(T)}{T} dT = 0$$

If rhs is a reservoir with fixed $T +$ thus $C(T)$

$$\Delta S_{tot} = \Delta S + \frac{Q_{rhs}}{T_{rhs}} = 0$$

Then $W_{rhs} = T_{rhs} \Delta S - \Delta U$

Example 1

maximum work from isothermal expansion of ideal gas?

$$\text{ideal gas } C = \frac{3}{2} \rightarrow \gamma = 5/3 \quad T_0 = 500\text{ K} \rightarrow T_i = 500\text{ K}$$

isothermal expansion $\rightarrow V_i = 2V_0$

energy balance: $\Delta U + \cancel{q_{rhs}} + w_{rhs} = 0 \quad w_{rhs} = -q_{rhs}$

entropy minimum: $\Delta S + \cancel{q_{rhs}}/T_{rhs} = 0 \quad q_{rhs} = -T_{rhs} \Delta S$

$$\Delta S = R \ln \left(\frac{V_i}{V_0} \right) = R \ln 2$$

$$w_{rhs} = T_{rhs} \Delta S = 500 R \ln 2$$

exactly what we got by integrating $-PdV$!!

Example 2

maximum work if our rhs is only @ 400 K ?

exactly same analysis $\Rightarrow w_{rhs} = 400 R \ln 2 < 500 R \ln 2$

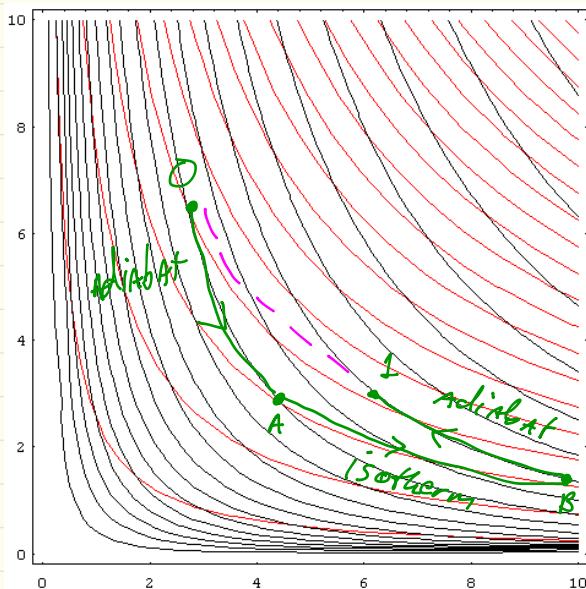
Begs the question how?? Have to find overall reversible path.

What's reversible? Adiabatic steps + isothermal steps w/ no T gradient.

Suggests • Adiabatic expansion to T_{rhs}

• Isothermal expansion to some TBD volume

• Adiabatic compression to final V + T .



$$O \rightarrow A \quad T_0 = 500 \text{ K} \quad T_A = 400 \text{ K}$$

$$\text{Adiabatic } \Delta U = -w_{\text{rev}} = cR(400 - 500) = -100cR$$

$$\Delta S = 0$$

Adiabat of an ideal gas: $T V^{\gamma-1} = \text{const}$

$$V_A = V_0 \left(\frac{T_0}{T_A} \right)^{1/\gamma-1} = V_0 \left(\frac{500}{400} \right)^{3/2} = V_0 \left(\frac{5}{4} \right)^{3/2}$$

$$B \rightarrow 1 \quad T_B = 400 \text{ K} \quad T_1 = 500 \text{ K}$$

exact opposite calculation

$$\Delta U = 100cR = -w_{\text{rev}} \quad \Delta S = 0$$

$$V_B = V_1 \left(\frac{T_1}{T_B} \right)^{1/\gamma-1} = 2V_0 \left(\frac{5}{4} \right)^{3/2} = 2V_A$$

aren't ideal gases nice?

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$$A \rightarrow B \quad T_A = T_B = 400\text{ K} \quad \Delta U = 0$$

$$\text{isothermal work } w_{\text{rms}} = R T \ln \frac{V_B}{V_A} = R \cdot 400 \ln 2$$

$$\mathcal{E}_{\text{rhs}} = -R \cdot 400 \ln 2$$

$$\Delta S = \frac{\mathcal{E}}{T} = R \ln 2$$

Add 'em up!

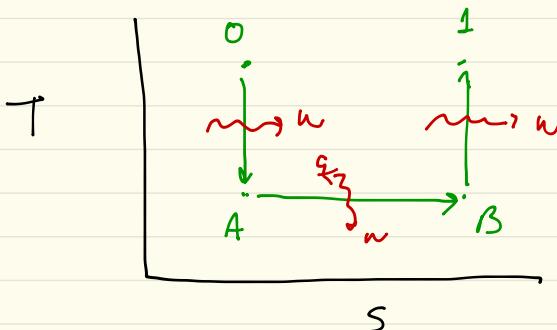
$$w_{\text{rms}} = 100c_R + 400R \ln 2 - 100c_R = \underline{400R \ln 2} \quad !!$$

$$\mathcal{E}_{\text{rhs}} = -400R \ln 2$$

$$\Delta U = -100c_R + 0 + 100c_R = 0$$

$$\Delta S = 0 + R \ln 2 + 0 = R \ln 2$$

Could have got more work if we had stopped @ 400K



Looks different on a "TS" diagram. Note $w =$
area under TS curve.

Example 3

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In these examples assumed T of rhs (or system) were constant. Wouldn't have to:

$$q_{rhs} = \int_{T_c}^{T_f} C_{rhs}(T) dT$$

$$q_{sys} = \int C_{sys}(T) dT$$

It's 5°C outside and I have a 1 kg bucket of 90°C water ($C_v = 75 \text{ J/mol K}$). How much work could I get out of cooling the water to ambient?

$$\Delta U_{ice} + q_{rhs} + w_{rhs} = 0 \quad (\text{Assume } H_2O \text{ does no P_r work in cooling down})$$

$$\Delta U_{ice} = \int_{T_0}^{T_f} C_v dT = -80 \text{ C}_v$$

$$\Delta S_{ice} + q_{rhs}/T_{rhs} = 0$$

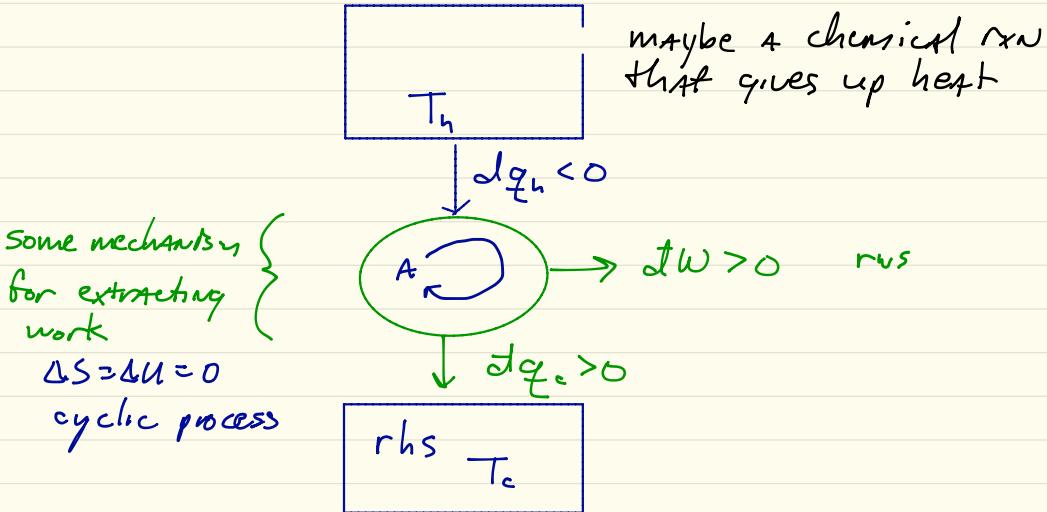
$$\Delta S_{ice} = \int \frac{C_v}{T} dT = C_v \ln T \Big|_{363}^{273} = C_v \ln \frac{273}{363} = -0.28 \text{ C}_v$$

$$q_{hi} = 278(0.28) \text{ C}_v$$

$$\begin{aligned} w_{rhs} &= -(\Delta U + q_{rhs}) = (80 - 0.28(278)) \text{ C}_v \\ &= 2.16 \text{ C}_v \end{aligned}$$

Good level-in too ...

thermodynamic engine



Focus on work associated with heat rejection,
so assume $dW_u = 0$ (it just adds to work at
the end anyway).

$$dS_{\text{tot}} = dS_h + dS_c = \frac{dq_u}{T_h} + \frac{dq_c}{T_c} \geq 0$$

2nd law

$$dq_c \geq -dq_h \left(\frac{T_c}{T_h} \right)$$

$$dw = -dq_h - dq_c \leq (-dq_h) \left(1 - \frac{T_c}{T_h} \right)$$

$$\frac{dw}{(-dq_h)} \leq 1 - \frac{T_c}{T_h}$$

E_e

If only we had
a lot of $T_c = 0$
Around!

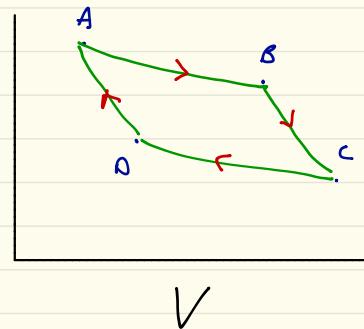
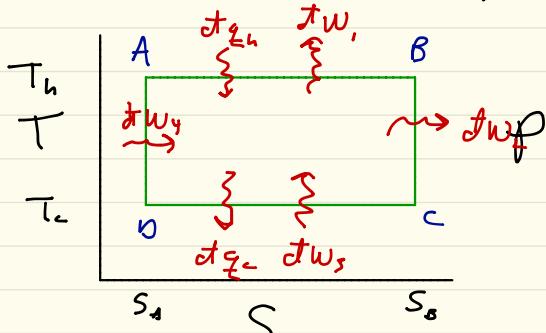
What we have essentially shown is that it is impossible to convert some amount of heat into an equivalent amount of work. The maximum amount of work is given by

$$W_{\max} = q \left(1 - \frac{T_c}{T_h}\right)$$

How much work you can really get out depends on the details of the "engine." This is an auxiliary device that converts incoming heat to work and somewhat less heat.

Must operate cyclically, so the engine returns to its original state and doesn't enter overall energy balance. Further, should not generate any additional entropy.

Carnot cycle represents optimally efficient way of converting heat to work. Involves the use of an auxiliary fluid



Steps are all quasi-static and reversible

$A \rightarrow B$ isothermal expansion

fluid in contact with system takes in heat ΔQ_h and produces work ΔW_1 , to rws

$B \rightarrow C$ Adiabatic expansion

fluid in contact w/rws produces additional work ΔW_2 until T drops to T_c

C \rightarrow D isothermal compression

fluid in contact w/ rhs rejects heat dq_c
as it is compressed until the entropy matches
state A

D \rightarrow A adiabatic compression

isolated fluid now is further compressed
until T returns to T_h

heat taken in is $q_h = T_h(S_B - S_A)$
(Area under AB line)

heat rejected is $q_c = T_c(S_B - S_A)$

By energy balance $\sum dw = dq_h - dq_c = (T_h - T_c)\Delta S$

$$\text{efficiency} = \frac{dw}{dq_h} = \frac{(T_h - T_c) \Delta S}{T_h \Delta S} = 1 - \frac{T_c}{T_h}$$

The Carnot cycle is thus maximally efficient

If we know the properties of the particular working fluid, could plot points on P-V or T-V diagrams as pairs of isotherms and adiabats.

Integrating along each leg gives work, heat, entropy change along each. Regardless of fluid we choose, always get same efficiency.

Book works through ideal monoatomic gas case.

Quick, quick... what is the power output of a Carnot engine?

$$\text{Power} = \frac{W}{t}$$

reversible

$$Q-S \rightarrow t \rightarrow \infty$$

T transfer across $\Delta T = 0$

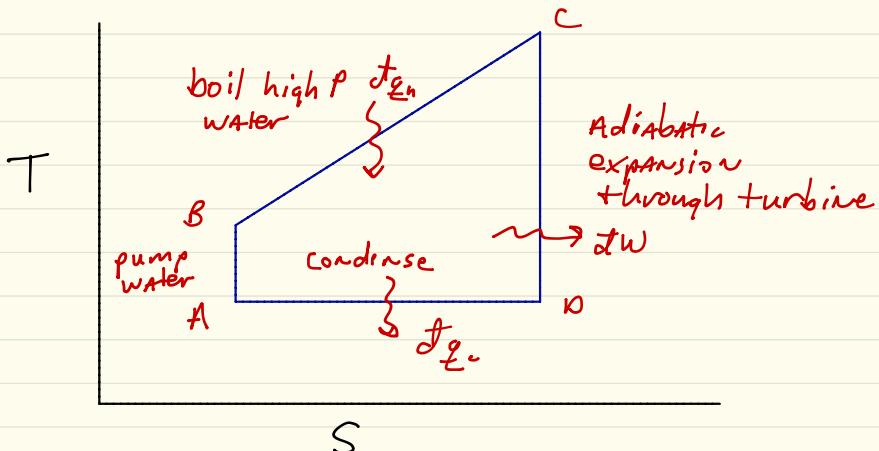
$\rightarrow 0 !!$

Not very useful. Real engines must be operated at some compromise between efficiency, power, cost, ... Heat transferred across finite T difference

Real engines generate extra entropy in the environment over ideal (Carnot) minimum

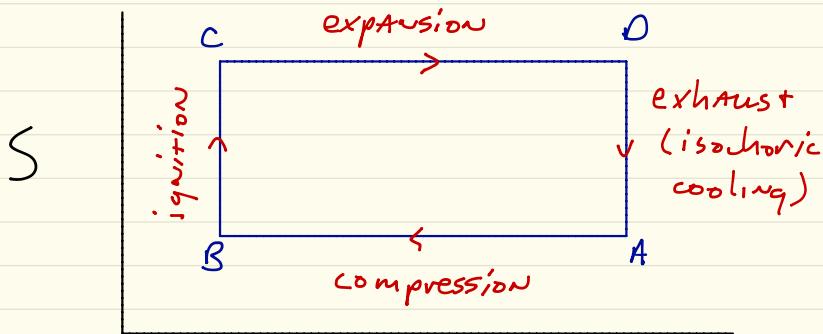
Other cycles

Rankine cycle - power generation
~ Carnot



$B \rightarrow C, D \rightarrow A$ ~isobaric for practical reasons

Otto cycle - SI engine, v. approximately



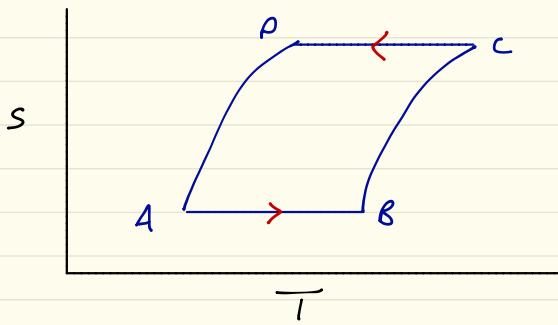
V

$$\eta_{\text{Otto}} = 1 - \left(\frac{V_B}{V_A} \right)^{\gamma-1}$$

$\gamma = C_p / C_v$

$\eta < \eta_{\text{carnot}}$ compression ratio

$$S(T, V, N) = c N R \ln \frac{T}{T_0} + N R \ln \frac{V}{N V_0} + N s_0$$



refrigerator

run everything
the other
direction

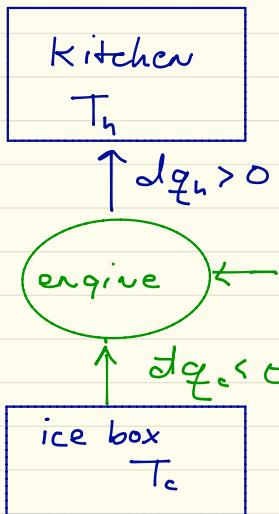


Figure of merit now $\frac{-dQ_c}{dW}$, coefficient of performance

$$dW = -dQ_h - dQ_c \leq (-dQ_c) \left(1 - \frac{T_h}{T_c}\right)$$

$$COP = \left(\frac{-dQ_c}{-dW}\right) \leq \frac{T_c}{T_h - T_c}$$

As $T_c \rightarrow 0$, $-dW \rightarrow \infty$!!

Note COP can be > 1 ; it takes less than $A J$ of work to move $A J$ of heat! COP of a refrigerator ~ 2 or so depending on actual operation.