Q&A session

General physics II: Thermodynamics

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Chapters 1, 2 & 3 (T & gas laws)

Temperature is a measure of how hot/cold a system is (state variable)

Zeroth law of Thermodynamics: If two systems are in thermal equilibrium with a third system then they are in thermal equilibrium with each other.

Thermal expansion and thermal stress: Change of length/volume due to ΔT

$\Delta l = \alpha l_0 \Delta T$; $\Delta V = \beta V_0 \Delta T$ $(\beta \approx 3\alpha)$

$\Delta l = \frac{1}{E} P l_0$ → young's modulus ⟹ $P = \alpha E l_0 \Delta T$

State variables, only dependent on current state, describe at TD system

T, V, P, S, n, μ

Ideal gas law and real gases:

$PV = N k_B T$; $PV = n \overset{N_A \cdot k_B}{\overset{\|}{R}} T$

Chapters 1, 2 & 3 (T & gas laws)

"Can we go over the van der Waals equation?"

van der Waals equation:

modification for ideal gas law if volume of molecules is non-negligible & interactions between molecules are non-negligible

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nKT$$

a & b material constants

correction due to vol.

correction of P due to interaction

Chapters 4 & 5 (Statistical TD)

Kinetic gas theory: link between macroscopic (T, V, P, ...) and microscopic variables (e.g. velocities ...)

Applicable for ideal gas with large particle number, elastic collisions and random, isotropic velocities

Average kinetic energy of one ideal gas particle is related to macroscopic T

$$\langle K \rangle = m \frac{\langle v^2 \rangle}{2} = \frac{3}{2} k_B T$$

Microstates: properties of individual gas particles, equally probably

Macrostates: global properties (T, P, ...), sum of P of microstates

Thermal equilibrium in statistical TD: a system takes on the macroscopic configuration which maximises the number of microstates Ω — Most likely macrostate is thermal equilibrium $\frac{d}{dE_1}(\Omega_1 \Omega_2) = 0$

$\frac{d}{dE_2} \log \Omega_2 (E_2) = \frac{d}{dE_1} \log \Omega_1 (E_1)$ for box 1&2

Boltzmann arguement: $\frac{d}{dE} \log \Omega (E) = \frac{1}{k_B T}$

Chapters 4 & 5 (Statistical TD)

"Can we repeat the distribution of gas particle velocities and the probability to have a certain energy in a particular system?"

open to the Universe

Boltzmann factor (describes the P that a system has energy E):

$$P(E) \propto e^{-E/k_BT}$$

"accounts for the influence of taking E_1 from Universe on total # of microstates in Universe"

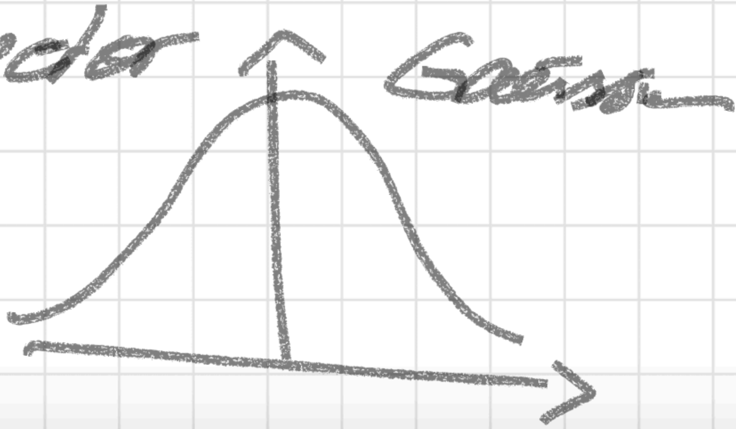
larger E taken out → e^{-E/k_BT} smaller → lower P

Applying Boltzmann factor to kinetic energy of gas ($E = \frac{m}{2}v^2$)

↳ P that gas particle has velocity vector

↳ P density for v between v & v + dv

$$P(v_x)\,dv = \sqrt{\frac{m}{2\pi k_B T}}\, e^{-\frac{m}{2k_BT} v_x^2}\, dv$$



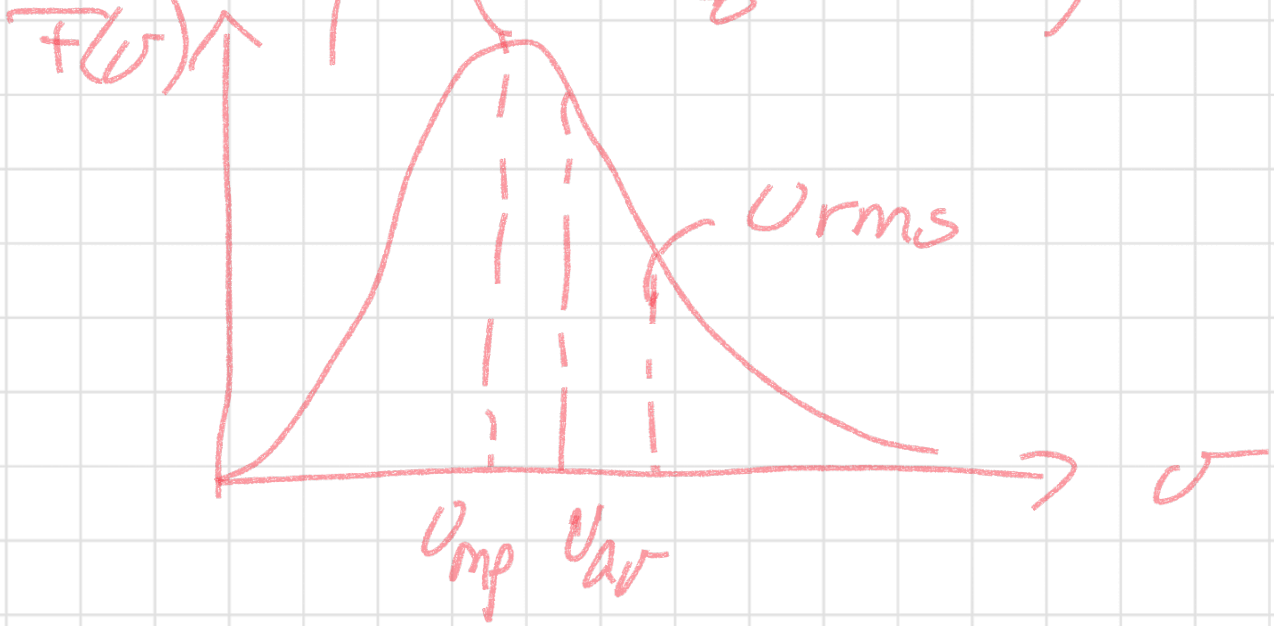
Chapters 4 & 5 (Statistical TD)

$\underline{v} \longrightarrow |\underline{v}|$

Maxwell-Boltzmann distribution (absolute velocity of particles):

$$F(v)\,dv = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{m}{2k_BT}v^2\right)dv$$

← integration of $F(v)\,dv$ over all



Particle velocities:

$$v_{mp} = \sqrt{\frac{2k_BT}{m}}$$

$$\left(\frac{d}{dv}F(v) = 0\right)$$

$$v_{avg} = \frac{2}{\sqrt{\pi}}\,v_{mp} \qquad \left(\int v\,F(v)\,dv\right)$$

$$v_{rms} = \sqrt{\frac{3}{2}}\,v_{mp} \qquad \left(\sqrt{\langle v^2\rangle}\right)$$

Chapters 4 & 5 (Statistical TD)

Why F(v) dv, why is there an dv??

$F(v)\,dv$ or $P(v)\,dv$: P that a particle has a speed between v & dv

$P(v)$ is not a probability but a prob. density!

i.e. Probability that $v \in [v, v+dv] = P(v)\,dv$

Maxwell-Boltzmann distribution:

$F(v)$ is the speed probability density $\left[\frac{1}{m/s}\right]$

dv is the width of speed intervall $[m/s]$

$F(v)\,dv$: P of particles between v & $v+dv$

Chapter 6 (Energy and heat)

Internal energy is the total amount of energy of all molecules, sum of thermal and potential energy

Thermal energy: kinetic energy due to translation, rotation and vibrations

Internal energy of ideal gas = thermal energy $E_{int} = E_{kin} = \frac{3}{2} N k_B T = \frac{3}{2} nRT$

Flow of energy via heat (due to T difference) and via work (due to PV work)

Sensible heat and latent heat: $Q_s = m \cdot c \cdot \Delta T$; $Q_L = mL$

Heat capacity: $Q_V = nC_V \Delta T$; $C_V = \frac{1}{n}\left(\frac{\partial E_{int}}{\partial T}\right)_V$

$Q_p = nC_p \Delta T$

Heat capacities of ideal gas: $C_p - C_V = R$; $C_V = \frac{3}{2} R$

Heat capacities of non-ideal gas via equipartition theorem: energy of molecules is shared equally between different degrees of freedom, each of which carries on average an energy of kT/2.

Chapter 7 (1. law & thermal processes)

First law and energy conservation:

$$\Delta E_{int} = Q - W \quad (W = \int P\,dV) \; ; \; dE_{int} = dQ - dW$$

Thermodynamic systems: isolated, closed, adiabatic, and open

Thermal processes: isothermal (dT=0), adiabatic (Q=0), isobaric (dP=0) & isovolumetric/isochoric (dV=0)

Change of internal energy in different processes:

Isochoric : $\Delta E_{int} = Q_V = nC_V \Delta T$

Isobaric : $\Delta E_{int} = nC_p \Delta T - P\Delta V$

for ideal gas: $\Delta E_{int} = nC_V \Delta T$

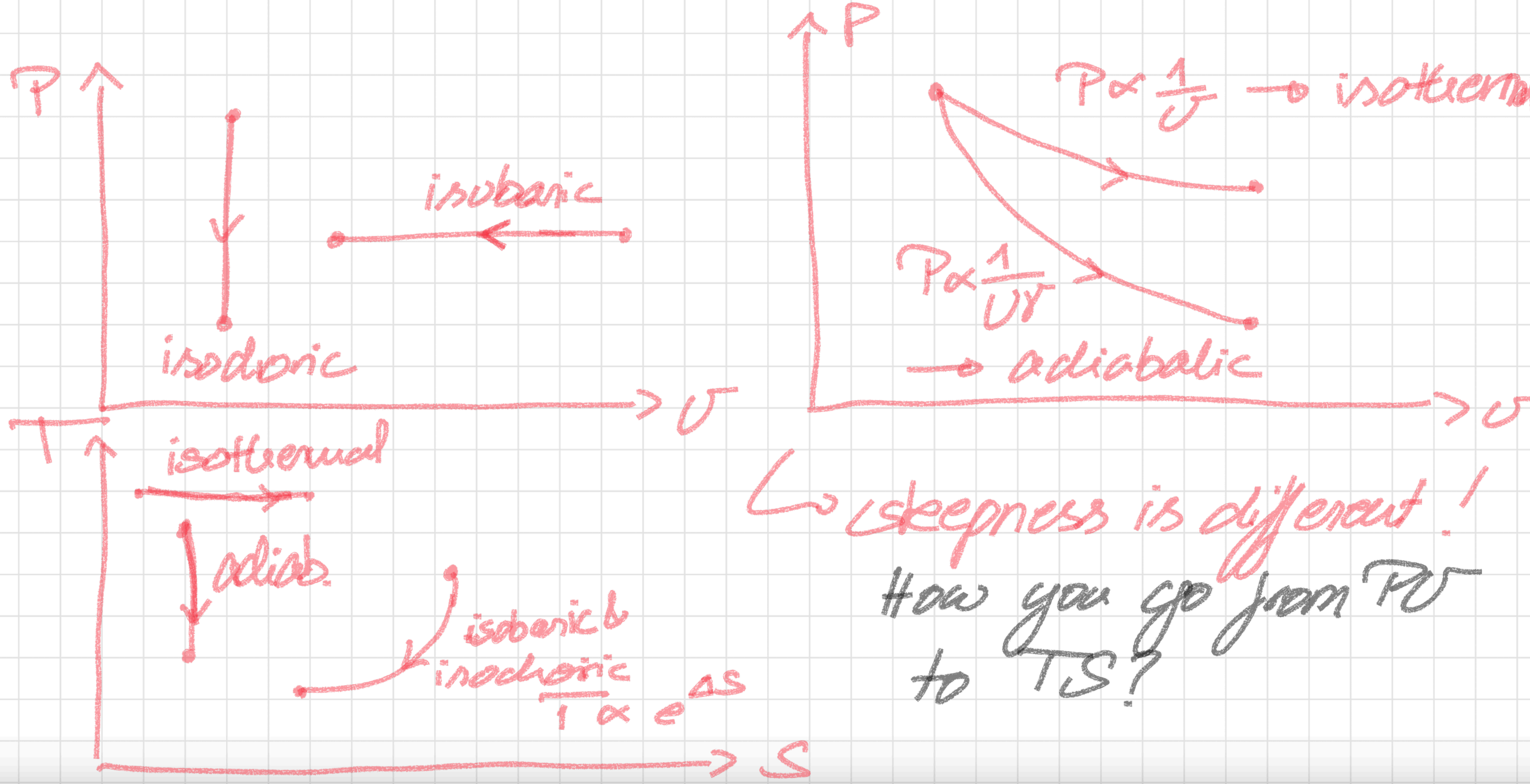
Isothermal: $\Delta E_{int} = 0$ if ideal gas $Q = W = P\Delta V$

Adiabatic : $Q = 0 \longrightarrow \Delta E_{int} = -W$

For ideal gas: $V^{\gamma} P = \text{const} \; ; \; \gamma = \frac{C_p}{C_V}$

Chapter 7 (1. law & thermal processes)

"I have a question about differentiating between the different processes on a diagram. If I am given a PV diagram, I can see if something is isochoric or isobaric quite easily, but is there a way to recognize from the diagram when the process is isothermal or adiabatic?"



↳ steepness is different!

How you go from PV to TS?

Chapter 8 (Entropy)

(Ir)Reversible process: any process that can (not) be reversed by changing signs of Q and W

Entropy is a state variable, entropy balance equation:

$$dS_{system} = \underset{\overset{\shortparallel}{\frac{dQ}{T}}}{dS_{env}} + \underset{\overset{\shortparallel}{\text{entropy prod. within system}}}{dS_{Prod}} \Rightarrow dS_{system} \geq dS_{env}$$

How can entropy help to distinguish between reversible and irreversible processes:

Reversible: $dS_{prod} = 0 \longrightarrow dS_{system} = dS_{env} = dQ/T$

Irreversible: $dS_{prod} > 0 \longrightarrow dS_{system} = dS_{env} + dS_{prod} = dQ/T + dS_{prod}$

Connection between first law and entropy:

$dE_{int} = dQ - dW$ & $dE_{int} = TdS - PdV$

But $dQ = TdS$ & $dW = PdV$ only for reversible p.

Chapter 8 (Entropy)

Connection between first law and entropy:

Why is $TdS = dQ$ and $PdV = dW$ only valid for reversible processes?

$TdS = dQ$ only valid for reversible processes because in irreversible processes, there is S production: $dS = dQ/T + dS\_prod \longrightarrow dQ < TdS$

Example: the entropy of a system can change even if there is no heat transfer at all: the mixing of two fluids with different physical properties inside a thermally isolated container: no heat flows into or out of the system, and yet its entropy changes because entropy is produced by the mixing of the substances. So here clearly $dQ = 0$ but $dS > 0$, for this irrev. process.

Because $TdS - PdV = dQ - dW$

$\hookrightarrow$ $dW \neq PdV$ if $TdS \neq dQ$

Chapter 8 (Entropy)

Second law: The entropy of a thermally isolated system cannot decrease over time: $dS >= 0$ (since isolated, $dS_{prod} >= 0$)

Third law: Entropy of a system converges against 0 for T —> 0, indpendent of all other properties of a particular system

Statistical interpretation of entropy:

Entropy of a macro state of a TD system is linked to the number of microstates:

$S = k_B \log \Omega$ "measure for disorder"

Second law: increasing S implies that system is evolving from more order (lower Ω) to less order (higher Ω) because it is more likely to have a higher Ω

Third law: S —> 0 for T—> 0: state of maximum order!

Chapter 9 (Thermal machines)

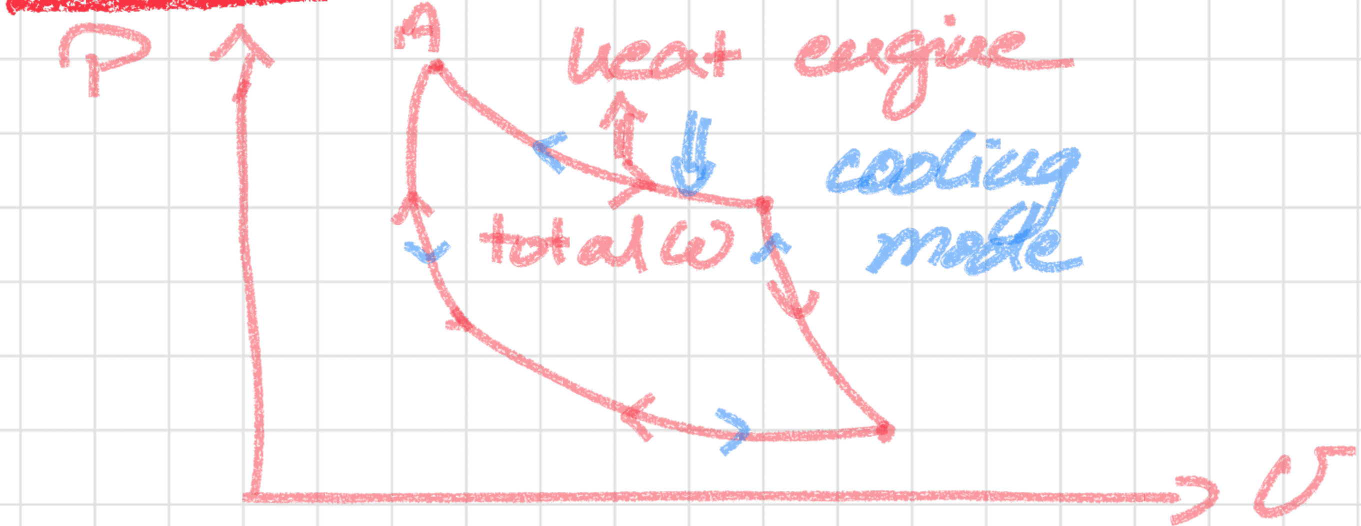
Thermal machine: TD system that performs a heat transfer between two thermal baths

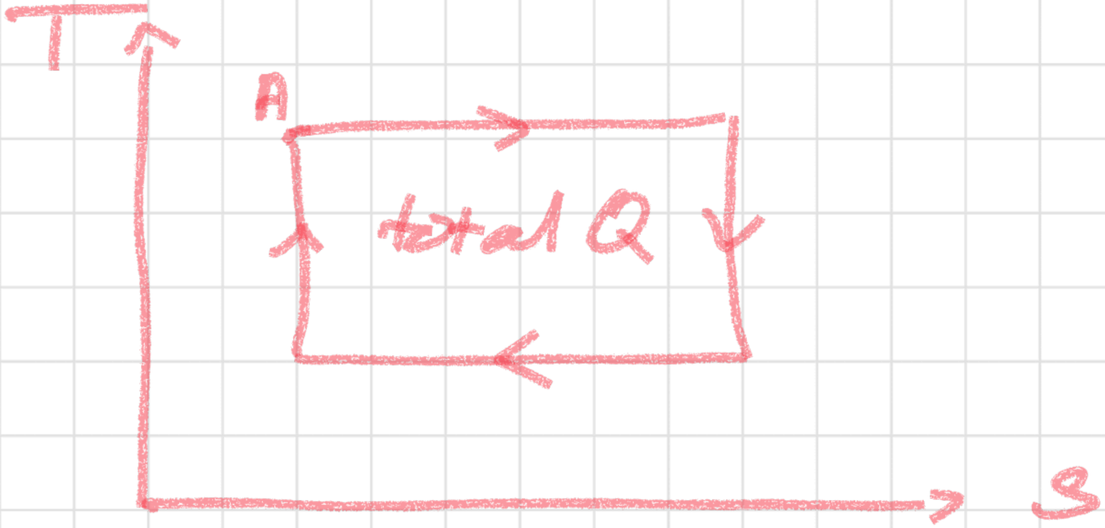
allowing for mechanical work being done by or on the system

by means of a periodically working machine (cycle process)

heat taken from hot reservoir, W done, heat given back to cold reservoir (or vice versa for cooling device/heat pump)

Carnot: two isothermal and two adiabatic processes





Engines: Stirling (two isothermal/isochoric); Otto (two adiabatic/two isochoric); Diesel (two adiabatic, one isobaric/isochoric) —> no need to know technical advantages/disadvantages

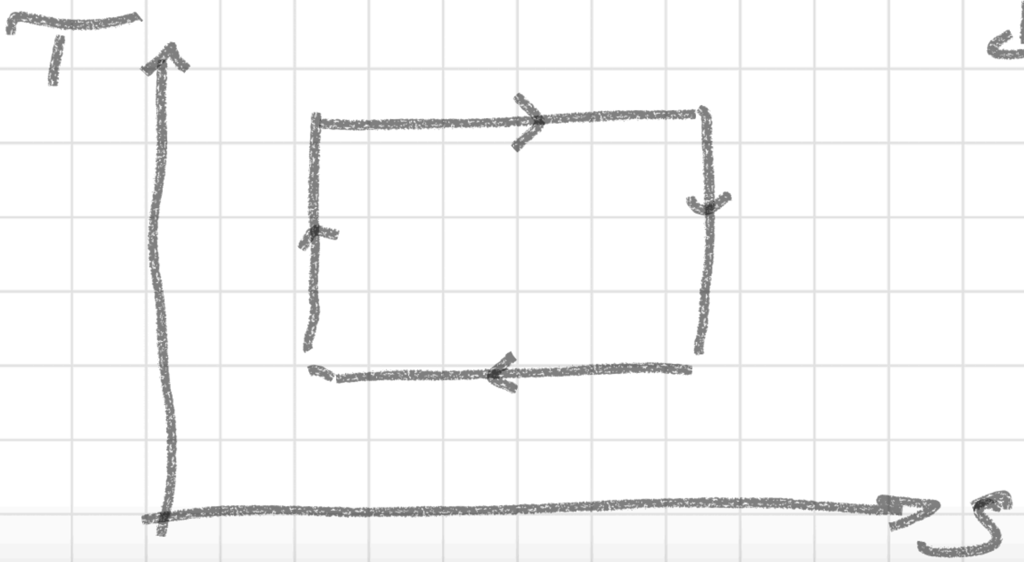
Chapter 9 (Thermal machines)

Question: "when to use PV & when TS diagram"

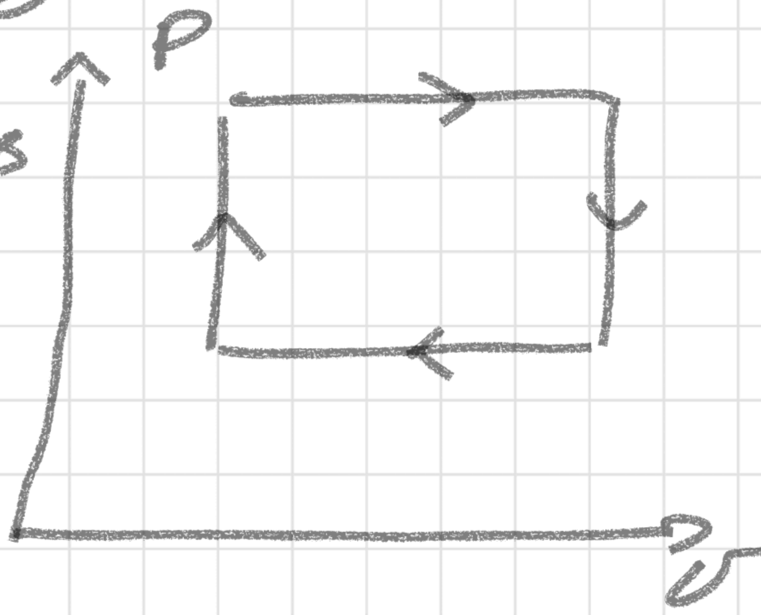
Depends on when Q/W calculation per cycle easier

E.g. Carnot cycle: TS diagram much simpler as you have to compute area of rectangle

$\oint dE_{int} = 0 \rightarrow$ Per cycle: $Q = -W$



But for 2 isochors
2 isobars
PV diagram easier...



Chapter 10 (TD potentials)

Basic relations: Gibbs fundamental relation:

$$dE_{int} = TdS - PdV + \sum_i \mu_i dn_i$$

chem. potential

# of moles

Euler relation:

$$E_{int} = TS - PV + \sum_i \mu_i n_i$$

Gibbs Duhem relation:

$$SdT - VdP + \sum n_i d\mu_i = 0$$

Chapter 10 (TD potentials)

TD potentials:

- Analogue role to potentials in mechanics
(state variables: derivatives of TD potentials, drive TD process
- Exact differentials: $f(x,y) \rightarrow df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy$

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$$ interchangeability of partial derivatives

- $dE_{int} = \underbrace{\left(\frac{\partial E_{int}}{\partial S}\right)_{V,n}}_{=T} dS + \underbrace{\left(\frac{\partial E_{int}}{\partial V}\right)_{S,n}}_{=-p} dV + \sum_i \underbrace{\left(\frac{\partial E_{int}}{\partial n_i}\right)_{S,V}}_{=\mu_i} dn_i$
- Natural variables of E_{int} are S, V, n

Chapter 10 (TD potentials)

"It would be great to go over the Legendre transforms once again. I don't get when we're supposed to use them and what they allow us to derive."

Why other TD potentials than E_{int}?

E_{int} good if processes happen at const V & const S

const V: $dE_{int} = dQ$; const S: $dE_{int} = \bar{d}W$

Other experiments: const P, const T or both

↳ Thus introduce other TD potentials similarly simple with a dif. set of natural variables!

↳ Legendre transform $g(y)$: $g(y) = f(x) - x\,y_{=\frac{df}{dx}}$

Chapter 10 (TD potentials)

"It would be great to go over the legendre transforms once again. I don't get when we're supposed to use them and what they allow us to derive."

* Enthalpy useful at const P & S

$H = H(P,S) = E_{int} + PV$

System kept at const P & S:

Heat added is equal to change in H

$dH = dQ$

Inhomogeneous system at const P & S:

↳ approach to thermal equilibrium

with $dH \leq 0$, equality at equilibrium

General note: Process/system with const variables

↳ go to that TD potentials where these are the natural variables

Chapter 10 (TD potentials)

"It would be great to go over the legendre transforms once again. I don't get when we're supposed to use them and what they allow us to derive."

* Free energy: $F(T,V) = E_{int} - TS$

Useful for processes at const T & V

System rigid ($dV=0$) & at const T

work on system = change in free energy

$dF = -dW$

Inhomogeneous rigid system at const T & V

approach to mechanical equilibrium

with $dF \leq 0$

Chapter 10 (TD potentials)

"It would be great to go over the legendre transforms once again. I don't get when we're supposed to use them and what they allow us to derive."

* Gibbs free enthalpy G:

$$G(T,P,n) = E_{int} - TS + PV = H - TS$$

Useful at const P & T, most chemical reactions at const P & T

↳ $G = \sum_i \mu_i n_i$ = chemical potential of TD system

If inhomogeneous system kept at const T & const P

↳ approach to chemical equilibrium via $dG \leq 0$

Exam: Friday, June 20th at 9.15am
check time and place!

3-4 exercises

1 DinA4 cheat sheet allowed (you write/print on both sides), nothing else

Good luck everyone!!