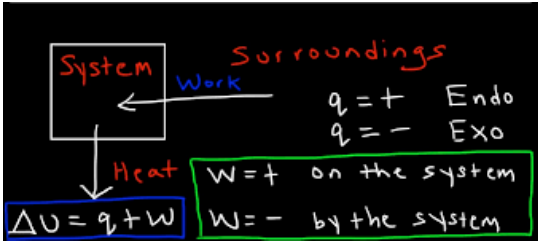
General Physics II: Thermodynamics

Prof. M. Hirschmann

Spring semester 2024



Recap… Chapter 6, Energy, heat and work in TD

- What is the internal and thermal energy? What is the internal energy of ideal gas?

- How can we describe the “flow of energy”?

- Conservation of energy: Delta $E_{int} = Q - W$ (main focus of this lecture!!)

Recap… Chapter 6, Heat capacity and calorimetry

- What is the relation between (sensible) heat and temperature?

- What is Calorimetry?

- Are heat capacities of gases the same at const V or at const P?

- What are the heat capacities of ideal gas? $C_P - C_V = R$ $\quad C_V = \frac{3}{2}R$

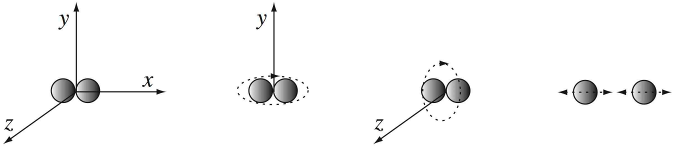
Recap… Chapter 6, Heat capacity for non-ideal gases & equipartition theorem

- If we consider non-ideal gas, which additional form of motion we should consider?

- How can we elegantly account for changes of heat capacities for non-ideal gas?

$$\frac{3}{2}R = 2.98\,\mathrm{cal/mol\cdot K},\ \frac{5}{2}R = 4.98\,\mathrm{cal/mol\cdot K},\ \frac{7}{2}R = 6.97\,\mathrm{cal/mol\cdot K}$$

Monatomic molecule: 3-translational kinetic energies, $n_f = 3$
Diatomic molecule: plus 2-rotational kinetic energies, $n_f = 5$
Diatomic molecule: plus1-vibrational kinetic and 1-vibrational potential energies, $n_f = 7$



Watch Equipartion theorem: https://www.youtube.com/watch?v=kzPHKchqkmY

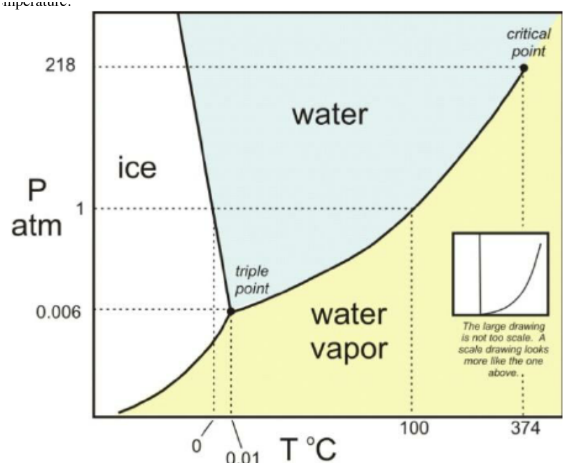
Recap… Chapter 6, Latent heat and phase transitions

- Which forms of heat do we have in TD?

- What is latent heat?

- What is a phase diagram in TD, and where comes latent heat in?

- What are the main characteristics of the phase diagram of water?



Content of this course — today's lecture

Lecture 1: —Chapter 1. Introduction
—Chapter 2. Temperature and zeroth law of thermodynamics

Lecture 2: —Chapter 3. Gas laws

Lecture 3: —Chapter 4. Statistical thermodynamics I: Kinetic theory of gas (slides in previous file)
—Mathematical Excursion — Preparation for Chapter 5.

Lecture 4: —Chapter 5. Statistical thermodynamics II (Boltzmann factor, Maxwell-Boltzmann distribution)

Lecture 5: —Chapter 6. Energy, heat and heat capacity

Lecture 6: —Chapter 7. First law of thermodynamics and thermal processes

Lecture 7: — Mock exam I *with Dr. Tress*

Lecture 8: —Chapter 8. Entropy and the second and third law of thermodynamics

Lecture 9/10: —Chapter 9. Thermal machines

Lecture 11: —Chapter 10. Thermodynamic potentials and equilibria

Lecture 12: —Mock Exam II *with Dr. Tress*
Lecture 13: —Chapter 11. Heat transfer (Conduction, Convection, Radiation)

Lecture 14: —Final review and open questions

7. First law of thermodynamics and thermal processes

- 7.1 First law of thermodynamics
- 7.2 Thermal processes
    - Isochoric processes
    - Isobaric processes
    - Isothermal processes
    - Adiabatic processes

7.1 First law of Thermodynamics

- Recap some definitions… ~ box of gas

- State variables: state of a system is characterised by physical properties that are described by a set of state variables (X_i, such as V, P, T, n,…). The state is entirely specified by the values of these state variables and it does not depend on the history of the system.

Q added to a system, W done by a system!
$\Rightarrow$ no state variables!

- Thermodynamic systems:
  - *open*: allows for matter and energy exchange with environment
  - *closed*: does not allow for matter exchange with environment (but for energy exchange)
  - *adiabatic*: does not allow for matter exchange and heat exchange with the environment (but for mechanical energy exchange)
  - *isolated*: does not allow for any interaction with the environment (no matter, no energy)

Last time, we started to discuss the first law of TD:

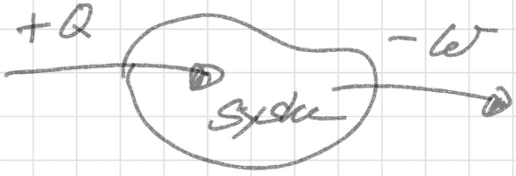
notation in Giancoli & official lecture notes

engineering view

$$\boxed{\Delta E_{int} = \underset{\uparrow}{Q} - \underset{\nwarrow}{W}}$$

heat added

work done by system



"−"

$W = P\Delta V$

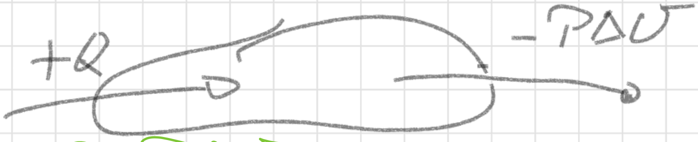
notation in Ansermet Brechet

physics view

Often, you find $\Delta E_{int} = Q + \underset{\uparrow}{W}$

$= -P\Delta V$

work done by the system



$\Delta E_{int} = Q - P\Delta V$

Energy conservation: sum of heat added & work done by system is equal to the change in E_{int}.

If we consider work done by the system as infinitesimal volume expansion dV

$$\hookrightarrow \; dW = P \cdot dV$$

$$\Rightarrow \boxed{dE_{int} = dQ - PdV}$$

differential form of 1. law

If $dV > 0$: work done by system

& $dE_{int} < dQ$; $dE_{int} = dQ - PdV$

If $dV < 0$: work done on system (force outside)

& $dE_{int} > dQ$; $dE_{int} = dQ + PdV$

This is valid for a closed system.

Other TD systems : * isolated : $\Delta E_{int} = 0$

simplification

No heat exch.
No work done
$Q = 0$; $W = 0$

* Adiabatic system , $Q = 0$

$$\Delta E_{int} = -W$$

* Open system: matter exchange, described by chemical work C : energy variation due to matter transfer between system & env.

$$\Delta E_{int} = Q - W - C$$

Example: using the first law!

2500 J of heat is added to closed system, & 1800 J of work is done on the system. What is the change of internal energy?

First law: $$\Delta E_{int} = Q - \underbrace{W}_{\text{work done on syst from envir} \; = -1800\,J}$$

$$\Rightarrow \Delta E_{int} = 2500\,J - (-1800\,J) = 4300\,J$$

Summary 7.1 First law of TD

- First law of Thermodynamics (energy conservation): heat added to the system, work done BY system ($W=P\Delta V$) is equal to the change in internal energy of a system:

$$\Delta E_{\text{int}} = Q - W \longrightarrow \text{closed syst}$$

- First law different thermodynamic systems (other than closed)
    - isolated: no heat and work transfer, $Q = 0$, $W = 0 \longrightarrow \Delta E_{int} = 0$
    - adiabatic: $Q = 0$, $\Delta E_{int} = - W$
    - open: matter exchange possible described by chemical work C: $\Delta E_{int} = Q - W - C$

Chapter 10 on TD potentials

7.2 Thermal processes

In the field of thermodynamics, a thermal process refers to any process or series of operations in which a thermodynamical system exchanges heat with its surroundings and/or undergoes a change in temperature.

work

Thermal processes can be categorized into several specific types of processes, each defined by how the system interacts with its environment and how certain thermodynamic properties change over the course of the process. Some common types of thermal processes include:

Isothermal ($\Delta T = 0$): while the state changes, the temperature is kept constant.
Adiabatic ($Q = 0$): process with no heat, i.e. thermally isolated system or a very fast process.
Isobaric ($\Delta P = 0$): while the state changes, the pressure is kept constant.
Isovolumetric ($\Delta V = 0$): while the state changes, the volume is kept constant.

Isochoric

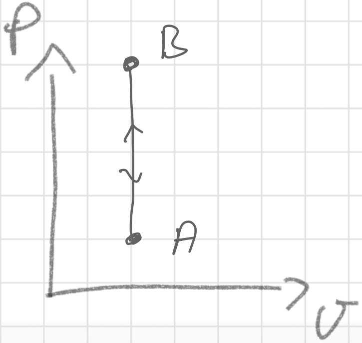
Below, we consider closed systems.

I. Isovolumetric / Isochoric processes $\Delta V = 0$

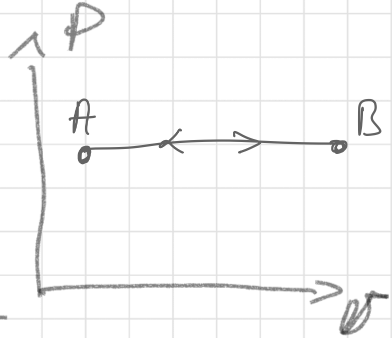
$$\Rightarrow \boxed{dE_{int} = dQ - \underset{0}{dW} = dQ = n C_V dT}$$

heat completely used to increase E_{int}

$$C_\theta \; C_V = \frac{1}{n}\left(\frac{\partial E_{int}}{\partial T}\right)_V = \frac{1}{n}\left(\frac{\partial Q}{\partial T}\right)_V$$



II. Isobaric processes ($\Delta P = 0$)



$$dE_{int} = dQ - P \cdot dV$$

$$dE_{int} = nC_p\,dT - P\,dV$$

Ideal gas: $C_p - C_v = R$ & $P\,dV = nR\,dT$

↳ $dE_{int} = n((C_v + R)\,dT - nR\,dT = nC_v\,dT$ (1)

for both isovolumetric & isobaric if ideal gas (because E_{int} of ideal gas is only dep. on T!)

Note: For ideal gas, any change of a state can be made as combinations of isovolumetric & isobaric processes

$\Longrightarrow$ change of E_{int} for a T change for any process is given by $\Delta E_{int} = nC_v\Delta T$.

III. Isothermal processes (T = const)

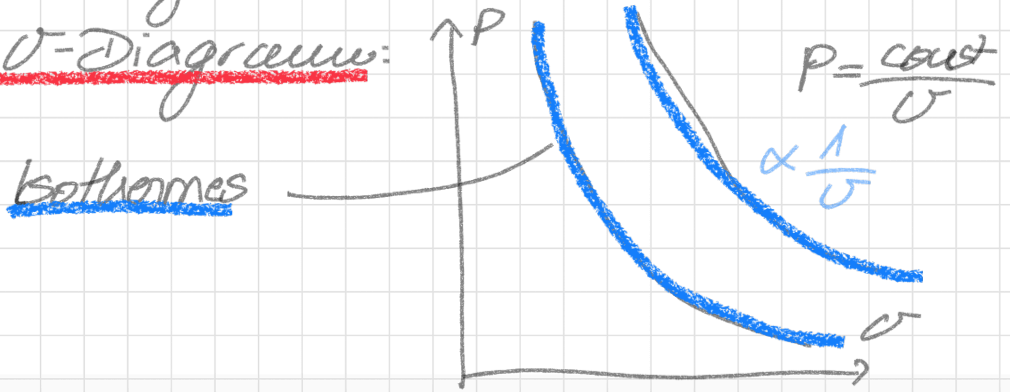
For ideal gas $\boxed{dE_{int} \equiv 0 \, !}$ (dE_{int} only dependent on T, kinetic gas theory, for ideal gas)

Heat added is completely transformed into work

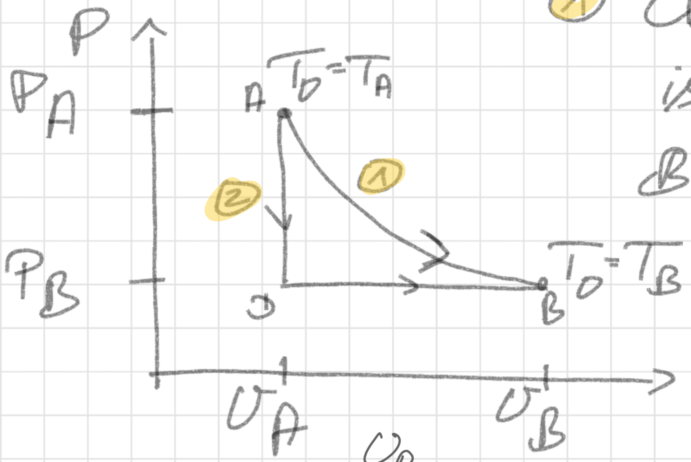
$$\hookrightarrow \quad \boxed{dQ = p\,dV}$$

Equation of state → Boyle-Mariotte law: $PV = \overset{nRT =}{const}$

Visualisation in P-V-Diagram:



Example for an isothermal process:



① Closed box of ideal gas is converted from state A to B via isothermal expansion.

Qu: What is the work done?

$\Delta E_{int} = 0 \Rightarrow Q = W$

$$W_{A \to B} = \int_{V_A}^{V_B} P\,dV$$

ideal gas law: $PV = nRT$

$$= \int_{V_A}^{V_B} \frac{nRT_0}{V}\,dV = nRT_0 \int_{V_A}^{V_B} \frac{dV}{V}$$

$$= nRT_0 \log V \Big|_{V_A}^{V_B} = nRT_0 \log \frac{V_B}{V_A} > 0$$

$$V_B > V_A$$

How does W done during ① compare to that in ②?

② : A → D → B

A → D : isochoric cooling ($\Delta V = 0$)

D → B : isobaric expansion ($\Delta P = 0$)

A → D : no work $W = 0$

D → B : $W_{D \to B} = \int_{V_A}^{V_B} P_B \, dV = P_B \int_{V_A}^{V_B} dV = P_B (V_B - V_A)$

$$W_{A \to D \to B} = 0 + P_B (V_B - V_A)$$

$$= \underbrace{P_B V_B}_{= nRT_0} \left(1 - \frac{V_A}{V_B}\right)$$

$$= nRT_0 \left(1 - \frac{V_A}{V_B}\right) \leq nRT_0 \quad \text{since } V_A < V_B$$

Recall: $W_{A \to B} = nRT_0 \log \frac{V_B}{V_A}$

$$\Longrightarrow \boxed{W_{A \to B} \neq W_{A \to D \to B}}$$

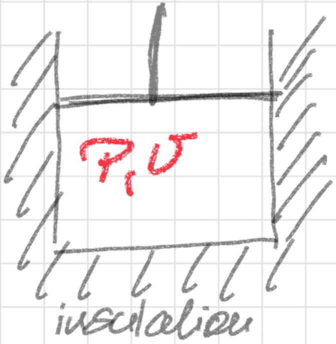
W is not a state variable!

$Q = W$ (if isothermal) → Q depends on the path in the PV diagram.

IV. Adiabatic processes (Q=0)

no heat exchange with environment

Classic example: (rapid) compression or expansion of gas inside a perfectly insulated cylinder



rapidly pushed piston inward → compressi

→ no heat can leave or enter system

(Bicycle pump)

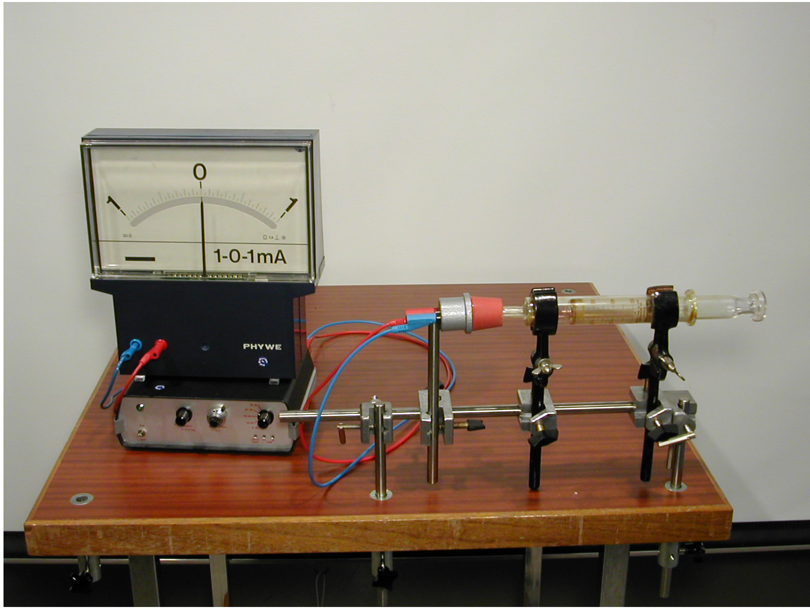
→ increase of P & T solely due to work done

Compression et détente adiabatique

https://www.youtube.com/watch?v=0TlewxjyKZ0

Set-up: A gas is injected into a piston. A thermocouple is placed inside the piston —> if T increases/decreases —> Voltage flows through thermocouple, V is measured

What happens when the piston is compressed/expanded?



Compression et détente adiabatique

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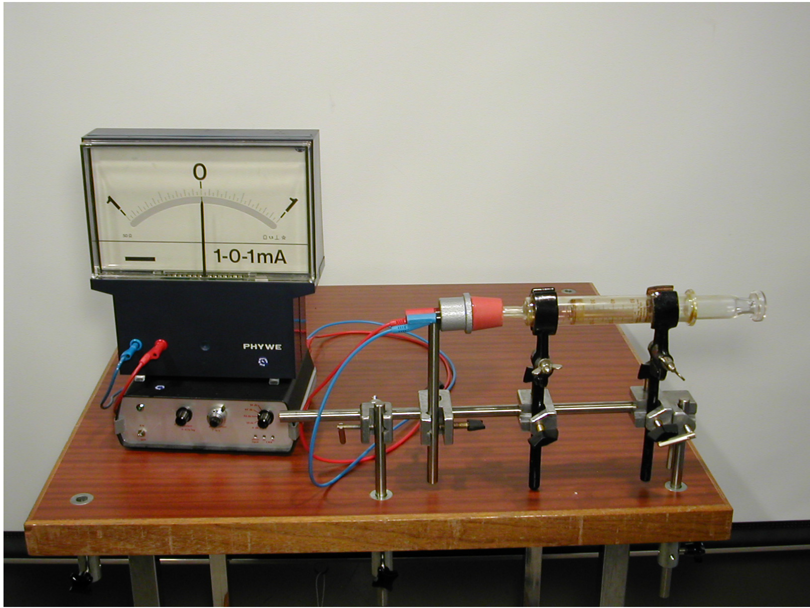
Set-up: A gas is injected into a piston. A thermocouple is placed inside the piston —> if T increases/decreases —> Voltage flows through thermocouple, V is measured

What happens when the piston is compressed/expanded?

Observation: When the piston is compressed (expanded), the temperature increases (decreases), and as a result, a voltage flows through the thermocouple. This voltage is then amplified and displayed, allowing the deduction of the temperature.

Key take-away: Process is adiabatic expansion, it is used in refrigerators, air conditioners, and refrigeration units to cool (in heat pumps). It is also used in scientific research to achieve very low temperatures.



How does P scale with V inside the cylinder?

How to draw an adiabatic process in the PV diagram

First law: $\Delta E_{int} = Q - W = Q - P\Delta V$

For ideal gas: $\Delta E_{int} = nC_v \Delta T$

$$\Rightarrow Q = \underset{\frac{nRT}{V}}{P}\Delta V + nC_v \Delta T \overset{\text{adiabatic}}{\overset{!}{=}} 0$$

$$\Rightarrow 0 = nC_v \Delta T + \frac{nRT}{V}\Delta V \quad \Big| : nRT$$

$$\Rightarrow 0 = \frac{C_v}{RT}\Delta T + \frac{\Delta V}{V} \quad \text{or} \quad 0 = \frac{C_v}{RT} dT + \frac{dV}{V} \quad (1)$$

Ideal gas law: $PV = nRT$ | differentiate on both sides

$$d(PV) = d(nRT) \Rightarrow V dP + P dV = nR dT$$

$$dT = \frac{dP\,V + P\,dV}{nR} \quad \text{into (1)}$$

$$\Rightarrow \quad 0 = \frac{C_v}{RT}\,\frac{dP\,V + P\,dV}{nR} + \frac{dV}{V}$$

PV

$$0 = \frac{C_v}{R}\left(\frac{dP\,\cancel{V}}{P\cancel{V}} + \frac{\cancel{P}\,dV}{\cancel{P}V}\right) + \frac{dV}{V}$$

$$0 = \frac{C_v}{R}\left(\frac{dP}{P} + \frac{dV}{V}\right) + \frac{dV}{V} \quad \Big|\cdot R$$

$$0 = C_v\,\frac{dP}{P} + \underbrace{(C_v + R)}_{= C_p \text{ (ideal gas!)}}\,\frac{dV}{V}$$

$$0 = C_v\,\frac{dP}{P} + C_p\,\frac{dV}{V} \quad \Big|\, C_v$$

$$0 = \frac{dP}{P} + \underbrace{\frac{C_p}{C_v}}_{:\gamma} \frac{dV}{V}$$

" adiabatic index "

$$0 = \frac{dP}{P} + \gamma \frac{dV}{V}$$

Recall: $\frac{d}{dx} \log x = \frac{1}{x}$

$$\frac{d}{dx}\left(\log f(x)\right) = \frac{\frac{d}{dx} f(x)}{f}$$

$$\Longrightarrow d(\log(f(x))) = \frac{d f(x)}{f}$$

Rewrite:

$$0 = d\log(P) + \gamma\, d(\log(V))$$

$$0 = d\log(P) + d\log(V)^{\gamma}$$ (sum of log = log of prod

$$0 = d \log (PV^{\gamma}) \quad \Big| \text{ integrate}$$

$$\text{const} = \log (PV^{\gamma}) \quad \Big| \exp$$

$$\underbrace{e^{\text{const}}}_{\text{const}'} = PV^{\gamma}$$

$\Longrightarrow$ Adiabatic process & ideal gas:

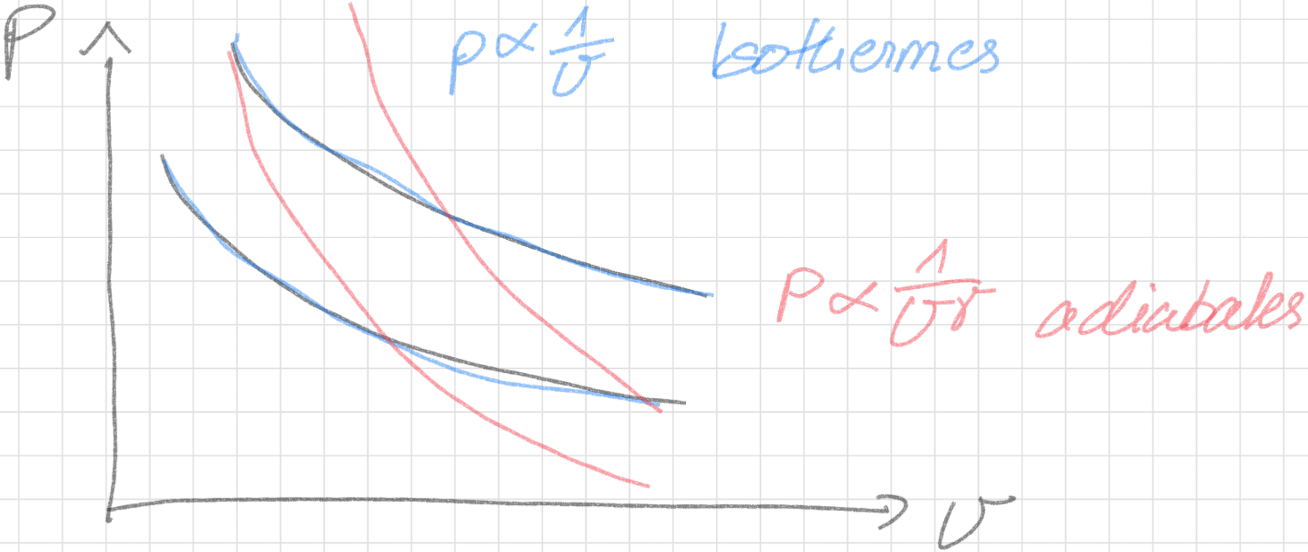
$$\boxed{PV^{\gamma} = \text{const}}$$

$\gamma > 1$ since $\gamma := \frac{C_p}{C_v}$; $C_p > C_v$

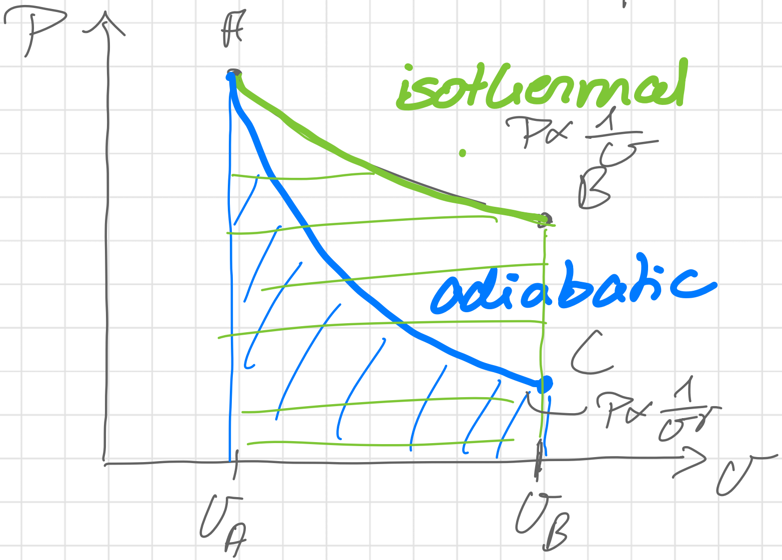
$$P = \frac{nRT}{V} \Longrightarrow nRT \cdot \frac{V^{\gamma}}{V} = \text{const}$$

$$\boxed{T \cdot V^{\gamma - 1} = \text{const}}$$

1 & 2: "Adiabatic equations" for ideal gas



Conceptual example:



Isothermal & adiabatic expansion of gas from initial V_A to final V_B

In which process is more work done?

More work done in the isothermal process

- Area under each curve represents the work

$$W = \int_{V_A}^{V_B} P\,dV \qquad W_{adiab} < W_{isoth.}$$

Example for adiabatic processes:

Air expands adiabatically from $P_1 = 2\,\mathrm{atm}$ & $V_1 = 2\ell$ at 20°C to $V_2 = 4\ell$. $\gamma_{air} = 1.4$

a) What is the final P_2?

b) What is the final T_2?

c) What is the work done by the gas?

a) $$P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \Longrightarrow P_2 = P_1 \left(\frac{V_1}{V_2}\right)^{\gamma}$$

$$= 2\,\mathrm{atm} \left(\frac{2\ell}{4\ell}\right)^{1.4} = 0.758\,\mathrm{at}$$

b) $$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \Longrightarrow T_2 = T_1 \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$= 293\,\mathrm{K} \cdot \left(\frac{2\ell}{4\ell}\right)^{0.4} = 222\,\mathrm{K} = -51\,^{\circ}\mathrm{C}$$

c) Calculation of work:

For ideal gas: $dE_{int} = nC_v\,dT$

First law: $dE_{int} = dQ - PdV$

$\Rightarrow dQ - PdV = nC_v\,dT$

$\Rightarrow dQ = nC_v\,dT + PdV = 0$

$\uparrow$ adiabatic

$\hookrightarrow PdV = -nC_v\,dT$

$$W_{adiab} = \int_{V_1}^{V_2} \underline{P}\,dV = -\int_{T_1}^{T_2} \underbrace{nC_v}_{\text{const}}\,dT = -nC_v \int_{T_1}^{T_2} dT$$

$$= -nC_v\,\Delta T = -\cancel{n}\,C_v\Big(\underset{\nwarrow\ \frac{P_2V_2}{\cancel{n}R}}{T_2} - T_1\Big)$$

Use $PV = nRT$ & $C_p - C_v = R$

$$W_{adiab} = -C_v\left(\frac{P_2V_2}{R} - \frac{P_1V_1}{R}\right) = -\frac{C_v}{C_p - C_v}\left(P_2V_2 - P_1V_1\right)$$

$$= -\frac{1}{\underset{\gamma}{\left(\frac{C_p}{C_v}\right.}-1}\left(P_2V_2 - P_1V_1\right)$$

$$\Longrightarrow W_{adiab} = -\frac{\left(P_2V_2 - P_1V_1\right)}{\gamma - 1}$$

Insert numbers: $W_{adiab} = -\frac{\left(0.758\,atm\cdot 4\ell - 2\,atm\cdot 2\ell\right)}{1.4-1}$

$$= 2.42\ \ell\cdot atm = 242\,J$$

$$\Delta E_{int} = Q - W$$

Work done by system on the environment

Simple TD processes & first law

Process	What is constant	First law, $\Delta E_{int} = Q - W$
Isothermal	$T = \text{const}$	$\Delta T = 0 \rightarrow \Delta E_{int} = 0 \rightarrow W = Q$
Isobaric	$P = \text{const}$	$Q = \Delta E_{int} + W = \Delta E_{int} + P\Delta V$
Isochoric	$V = \text{const}$	$\Delta V = 0 \rightarrow W = 0 \rightarrow \Delta E_{int} = Q$
Adiabatic	$Q = 0$	$\Delta E_{int} = -W$

Summary 7.2, thermal processes

- Isochoric/Isovolumetric $\boldsymbol{\Delta}$V = 0

$$\Delta E_{\mathrm{int}} = Q_{\mathrm{V}} = nC_{\mathrm{V}}\Delta T$$

- Isobaric $\boldsymbol{\Delta}$P = 0

$$\Delta E_{\mathrm{int}} = nC_{\mathrm{P}}\Delta T - P\Delta V$$

For ideal gas: $\Delta E_{\mathrm{int}} = nC_{\mathrm{V}}\Delta T$

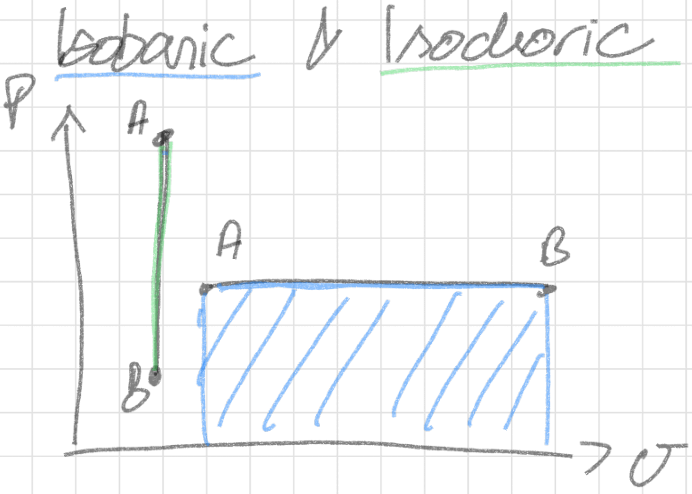
Note that here any change from one thermal state to another can be made as combinations of isochoric and isobaric processes, with $\Delta E_{\mathrm{int}} = nC_{\mathrm{V}}\Delta T$

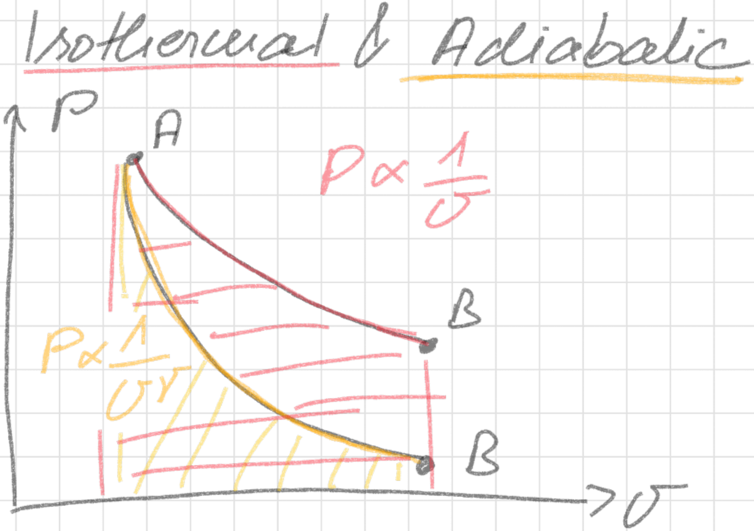
- Isothermal $\boldsymbol{\Delta}$T = 0 —> $\Delta E_{\mathrm{int}} = 0$ (if ideal gas) —> $Q = W = P\Delta V = nR\Delta T = const.$

- Adiabatic Q = 0 —> $\Delta E_{\mathrm{int}} = - W$

For ideal gas: $Q = P\Delta V + nC_V \Delta T$ —> $V^{\gamma}P = const.$

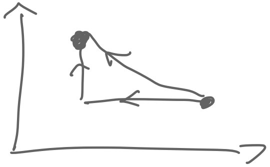
Summary 7.2, thermal processes in the PV-diagram





Work is area under the curve $\int_{V_A}^{V_B} P\,dV = W$

Conceptual questions



- An ideal monoatomic gas expands slowly to twice its volume (a) isothermally, (b) adiabatically, (c) isobarically. Plot each on a PV diagram. In which processes is ΔE_{int} the greatest and least? In which is W the greatest and the least? And in which is Q the greatest and the least?
- An ideal gas undergoes an isobaric compression and then an isenvolumetric process that brings it back to its initial temperature. Had the gas undergone one isothermal process instead (a) the work done on the gas would be the same; (b) the work done on the gas would be less; (c)…would be greater; (d) need to know the T of the isothermal process.
- An ideal gas undergoes an isothermal process. Which of the following statements are true? (i) no heat is added or removed from the gas. (ii) the internal energy of the gas does not change. (iii) the average kinetic energy of the molecules/gas particles does not change.
- In an isothermal process, 3700 J of work is done by an ideal gas. Is this enough information to tell how much heat has been added to the system? If so, how much? If not, why not?
- An ideal gas undergoes an adiabatic expansion. As a result (i) the T of the gas remains constant and the P decreases. (ii) both T and P of the gas decrease. (iii) the temperature of the gas decreases and the pressure increase. (iv) both T and V of the gas increase. (v) both the temperature and pressure of the gas increase.
- Think of your questions!

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