Thermodynamica 2

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Lecture 1

November 9, 2010

TU Delft
Delft University of Technology

Thermodynamica 2

- Studiehandleiding op blackboard
- Boek Moran&Shapiro (5e/6e editie) + extra materiaal blackboard
- Voorkennis: Thermodynamica 1 en wiskunde (integreren, differentiëren)
- Tentamen
    - Open vragen
    - Gesloten boek
    - Formuleblad zal worden uitgereikt op het tentamen
- Uitgewerkte opgaven op blackboard

- College 1 tm 9 → T.J.H. Vlugt (voornamelijk H11)
- College 10 tm 14 → P. Colonna (zie studiehandleiding)

- Begin op tijd met de voorbereiding van het tentamen!
- Is iets niet duidelijk, neem (op tijd) contact op met de docenten!!

Inhoud college 1 tm 9

- Evenwichten (bv vloeistof / damp)
- Relaties tussen thermodynamische grootheden
- Veranderingen van thermodynamische grootheden
- Wat te doen met systemen anders dan een ideaal gas

- Breng papier en pen mee naar het college
- Print het formuleblad uit

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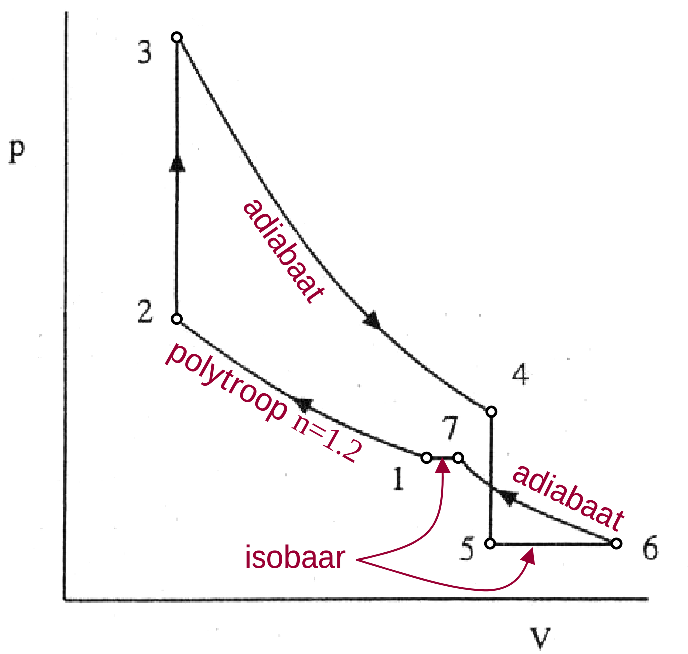
Vandaag: samenvatting ThermoI

• 1e hoofdwet voor open en gesloten systemen	2.1-2.5, 4.1-4.3
• Warmte en arbeid, toestandsgrootheid en procesgrootheid	2.1-2.5
• Enthalpie	3.3.2
• 2e hoofdwet voor open en gesloten systemen	6.1-6.7
• Fasediagram van zuivere componenten	3.1-3.2
• Ideale gaswet, toestandsvergelijkingen	3.1-3.5
• Afwijkingen van ideaal gasgedrag	3.4, 11.1

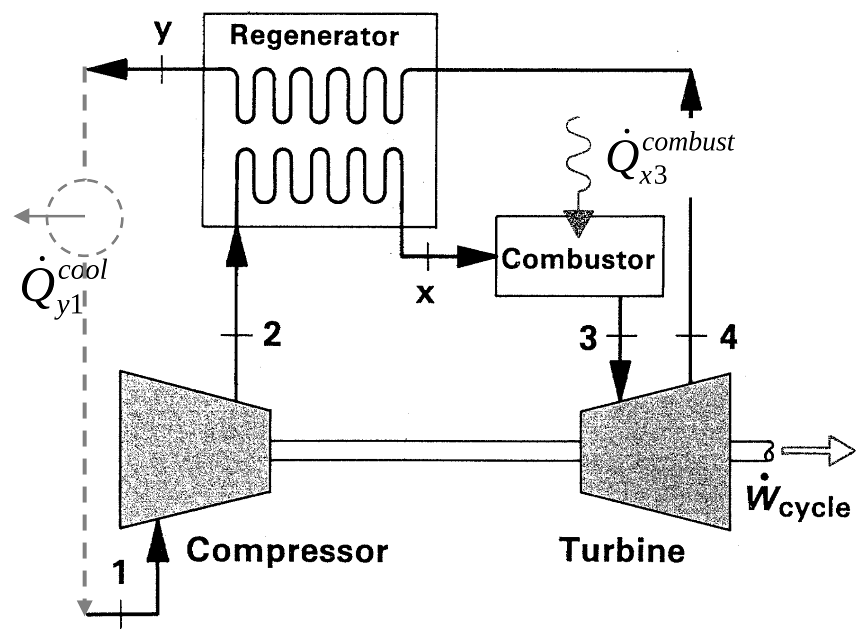
- Homework: make the following exercises: 2.17 2.36 2.41 2.49 3.16 3.63 4.29

The 1st law of Thermodynamics

closed systems	open systems
$$dU = \delta Q - \delta W$$	$$\frac{dE_{cv}}{dt} = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m}_i\left(h_i + \frac{V_i^2}{2} + gz_i\right) - \dot{m}_e\left(h_e + \frac{V_e^2}{2} + gz_e\right)$$
Thermodynamics I: applied e.g. to combustion cycle processes (modified) Otto cycle	Thermodynamics I: applied e.g. to compressors etc. in Brayton cycle



$$\dot{Q}_{2x} = -\dot{Q}_{4y}$$



Quantities and concepts in Thermodynamics

first law $$dU = \delta Q - \delta W$$

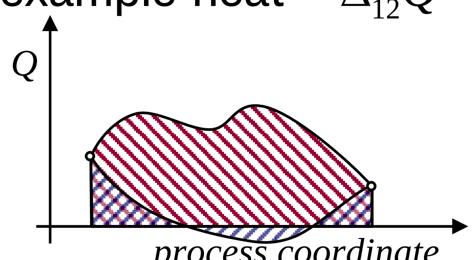
(1) → dU, (2) → δQ

State property (toestandsgrootheid), $A(v_1,\ldots v_N)$

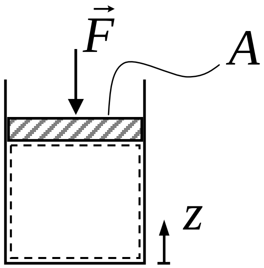
- with differential operator (1) (total differential)
- A does not depend on process path, but only on variables $(v_1,\ldots v_N)$
- for state properties $\oint dA = 0$
- for example $U(V,T)$, $p(T,V)$, $T(p,V)$, $V(T,p)$, …
- for state properties $\Delta_{12}U = \int_{'1'}^{'2'} dU = U(V_2,T_2) - U(V_1,T_1)$

Process quantities (procesgrootheid)

- with differential operator (2) (inexact differential)
- process quantities depend on the process path
- for example heat $\Delta_{12}Q = \int_{'1'}^{'2'} \delta Q$ **not equal to** $Q(\text{"}state\,2\text{"}) - Q(\text{"}state\,1\text{"})$



Volume-work



pressure $p = \frac{|\vec{F}|}{A}$

work $\Delta_{12}W = \int \vec{F} \bullet d\vec{s} = \int p\, A\, dz = \int p\, d(Az) = \int p\, dV$

$\Rightarrow$ work through volume change $\Delta_{12}W = \int_{V_1}^{V_2} p\, dV$

- W>0 work is done ***by*** the system
- W<0 work is done ***on*** the system

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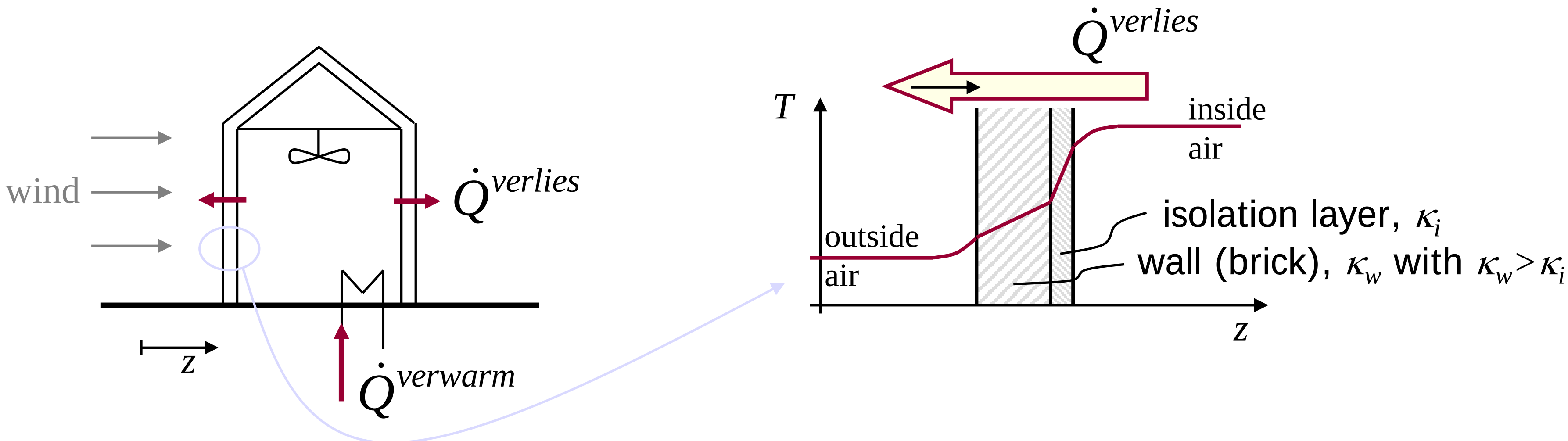
Energy transfer by heat

- energy transfer of heat is due to a temperature-difference (temp.-gradient)
- the energy transfer is in the direction of decreasing temperature



- energy transfer by heat conduction follows the Fourier's law $\dot{Q} = -\kappa A \dfrac{dT}{dz}$

heat-conductivity coefficient κ
(warmtegeleidingscoëfficiënt)

surface area

- an energy-package of heat is defined as $\Delta_{12} Q = \int_{t_1}^{t_2} \dot{Q}\, dt$

- $\Delta_{12} Q$ depends on the process path, it is a process quantity (no state property)
- $\delta Q = \dot{Q} dt$ is an inexact differential

1^{st} Law of Thermodynamics

Each **closed** system has a property *U*, the **internal energy**, for which:

- (neglect differences in KE and PE)
- the change in *U* for an **adiabatic** process is equal to the work *W* by the system;
- the added heat *Q* for a **non-adiabatic** process is given by

$$\boxed{Q = U_2 - U_1 + W}$$

- heat & work are process quantities; internal energy U is a state quantity

- Q>0 heat is transferred ***<u>to</u>*** the system
- Q<0 heat is transferred ***<u>from</u>*** the system

- W>0 work is done ***<u>by</u>*** the system
- W<0 work is done ***<u>on</u>*** the system

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1^{st} Law of Thermodynamics

$$Q = U_2 - U_1 + W$$

Adiabatic process: Q=0

- Q>0 heat is transferred ***to*** the system
- Q<0 heat is transferred ***from*** the system

- W>0 work is done ***by*** the system
- W<0 work is done ***on*** the system

The Enthalpy

$$H \equiv U + pV$$

$$h \equiv u + pv$$

$$dh = du + d\left(pv\right) = du + pdv + vdp$$

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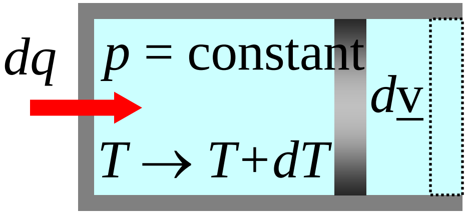
Adding heat while keeping the pressure constant

•Recall the first law: $du = \delta q - \delta w = \delta q - pdv$



•Enthalpy: $H \equiv U + pV$ $\qquad h \equiv u + pv$

•First law in terms of enthalpy:

$$dh = \delta q + vdp$$

•Adding heat at constant pressure $dh = \delta q$

•Definition of heat capacity at constant pressure: (here: in units of [$J\ mol^{-1}\ K^{-1}$])

$$c_p \equiv \left(\frac{\partial h}{\partial T}\right)_p$$

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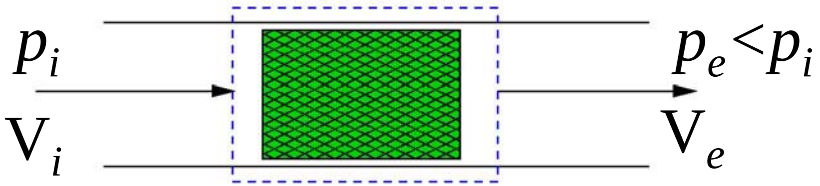
Energy balance for an open system

$$\frac{dE_{cv}}{dt} = \dot{Q}_{cv} - \dot{W}_{cv} + \dot{m}_i\left(h_i + \frac{\mathrm{V}_i^{\,2}}{2} + gz_i\right) - \dot{m}_e\left(h_e + \frac{\mathrm{V}_e^{\,2}}{2} + gz_e\right)$$

with $$E_{cv} = \int_V \rho\left(u + \frac{\mathrm{V}^2}{2} + gz\right)dV$$

Throttle (Smoorklep)



1[st] law for stationary open system

$$\dot{W}_{cv} = \dot{Q}_{cv} + \dot{m}\left((h_i - h_e) + \left(\frac{V_i^{\,2}}{2} - \frac{V_e^{\,2}}{2} \right) + g(z_i - z_e) \right)$$

adiabatic process ($\dot{Q}_{cv}=0kW$) and with $\dot{W}_{cv}=0kW$ and $g(z_i\text{-}z_e) << (h_i\text{-}h_e)$

$$h_i + 1/2\, V_i^{\,2} = h_e + 1/2\, V_e^{\,2}$$

when the kinetic energy is negligible, i.e. $1/2\left(V_i^{\,2} - V_e^{\,2}\right)$ low compared to $c_p(T,p)$

$$h_i = h_e$$

$\approx$1 kJ/(kg K)
=1000 $(m^2/s^2)K^{-1}$
order of magnitude

for ideal gases $h(T,P)$ is only $h(T)$ $\Rightarrow$ $T_i=T_e$ for ideal gases ONLY

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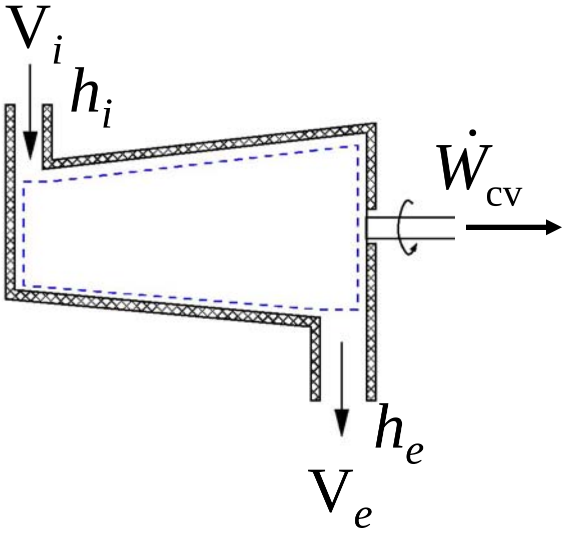
Turbine



1^{st} law for stationary open system

$$\dot{W}_{cv} = \dot{Q}_{cv} + \dot{m}\left(\left(h_i - h_e\right) + \left(\frac{V_i^{\,2}}{2} - \frac{V_e^{\,2}}{2} \right) + g\left(z_i - z_e\right) \right)$$

heating/cooling is often not realized, so that the process is adiabatic ($Q_{cv}=0kW$) and with $g(z_i\text{-}z_e) << (h_i\text{-}h_e)$ and $1/2(V_i^2\text{-}V_e^2) << (h_i\text{-}h_e)$ we get

caution:
this is not applicable for liquid systems, say in hydro-power plants

to be checked

$$\dot{W}_{cv} = \dot{m}\left(h_i - h_e\right)$$

$\Rightarrow$ as a result of the work obtained from the system, the enthalpy of the working-fluid is reduced (and therewith the working-fluids temperature $T_e<T_i$)

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The second law of Thermodynamics

- the 2nd law for closed systems in differential form

$$dS = \frac{\delta Q}{T} + \delta\sigma \qquad \delta\sigma \geq 0 \qquad \text{(closed system)}$$

$\delta\sigma = 0$	entropy production for reversible processes
$\delta\sigma > 0$	entropy production of non-reversible processes (due to irreversibilities)

- The entropy S is a state property. The entropy production σ is a process quantity, NOT a state property

- The entropy production $T_0 \cdot \sigma$ is the "lost work" of the system, i.e. the non-utilized work potential

- For a close-to-ideal process (close to reversible), σ approaches zero (but in practice does not reach zero)

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Second law for open systems

For closed systems we have

$$dS = \frac{\delta Q}{T} + \delta\sigma$$

entropy production $\delta\sigma \geq 0$ $\begin{cases} \delta\sigma = 0 \text{ for reversible processes} \\ \delta\sigma > 0 \text{ for irreversible processes} \end{cases}$

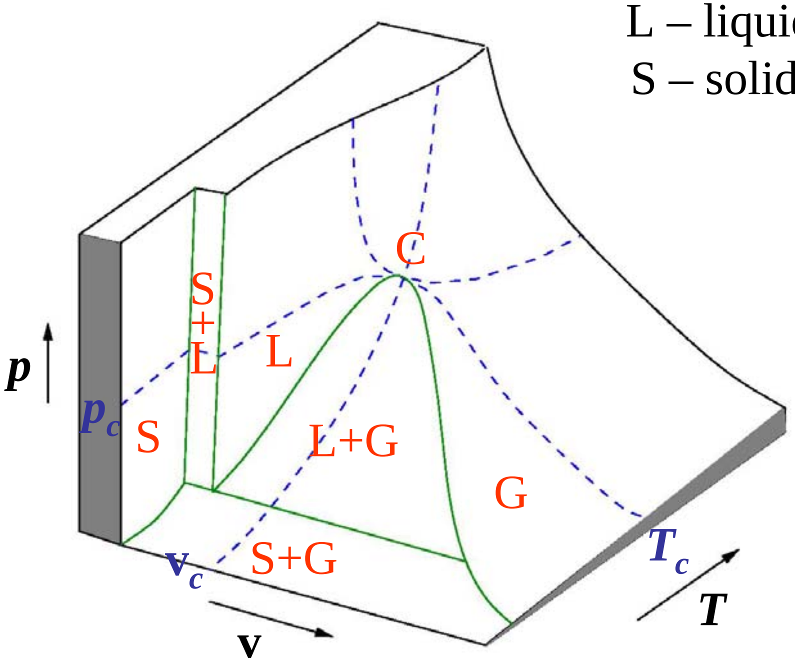
For open systems (control volume) there is also

'entropy carried with mass' entering and 'entropy carried by mass' leaving, so that

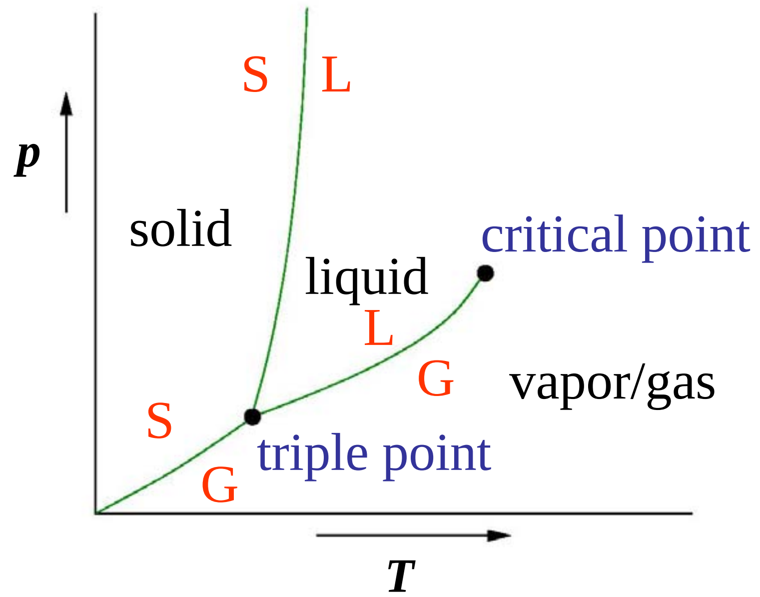
$$\frac{dS_{cv}}{dt} = \frac{\dot{Q}_{cv}}{T_{trans}} + \dot{m}_i s_i - \dot{m}_o s_o + \dot{\sigma}_{cv} \quad \text{with} \quad \dot{\sigma}_{cv} \geq 0$$

temperature at which the heat transport $\dot{Q}_{cv}$ occurs

Phase diagram



G – vapor
L – liquid
S – solid



Equation of state of Ideal Gases

$$pV = n\bar{R}T \qquad p\bar{v} = \bar{R}T \qquad \bar{v} = \frac{V}{n}$$

$$\bar{R} = 8.314471 \frac{J}{mol\,K}$$

p	pressure $[Pa]$
V	volume $[m^3]$
T	temperature $[K]$
n	amount of substance $[mol]$

1 mol contains N_A = 6.0221367×10^{23} molecules

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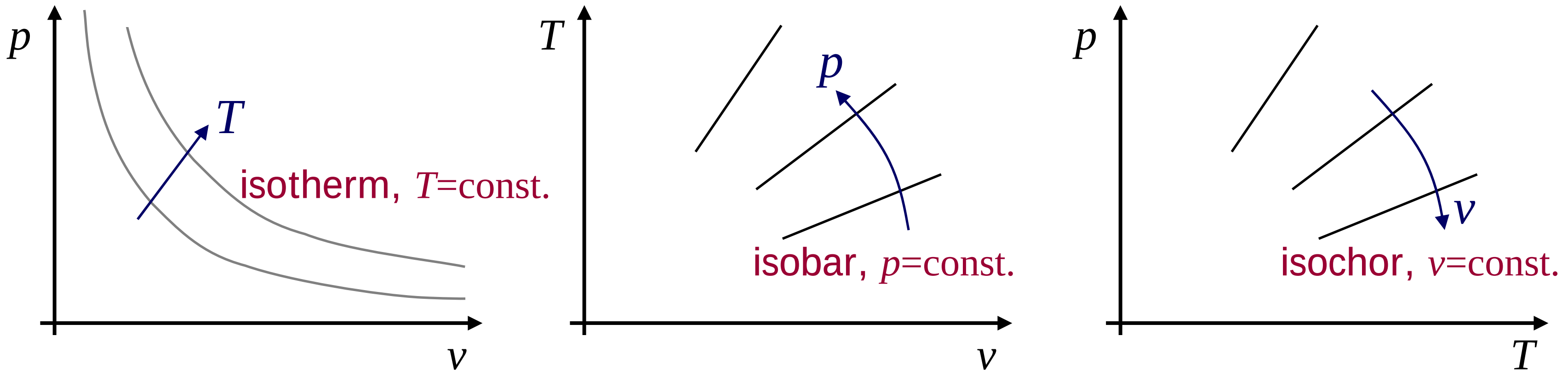
The “iso”-diagrams for ideal gases

The relation between 2 of the 3 properties $\{p,v,T\}$ can be visualized in state diagrams



Dealing with “real” gases

compressibility factor: $$Z = \frac{p\bar{\mathrm{v}}}{\bar{R}T}$$

ideal gas limit: $$\lim_{p \to 0} Z = 1$$

reduced pressure and **reduced** temperature: $$p_{\mathrm{R}} = \frac{p}{p_c}, \quad T_{\mathrm{R}} = \frac{T}{T_c}$$

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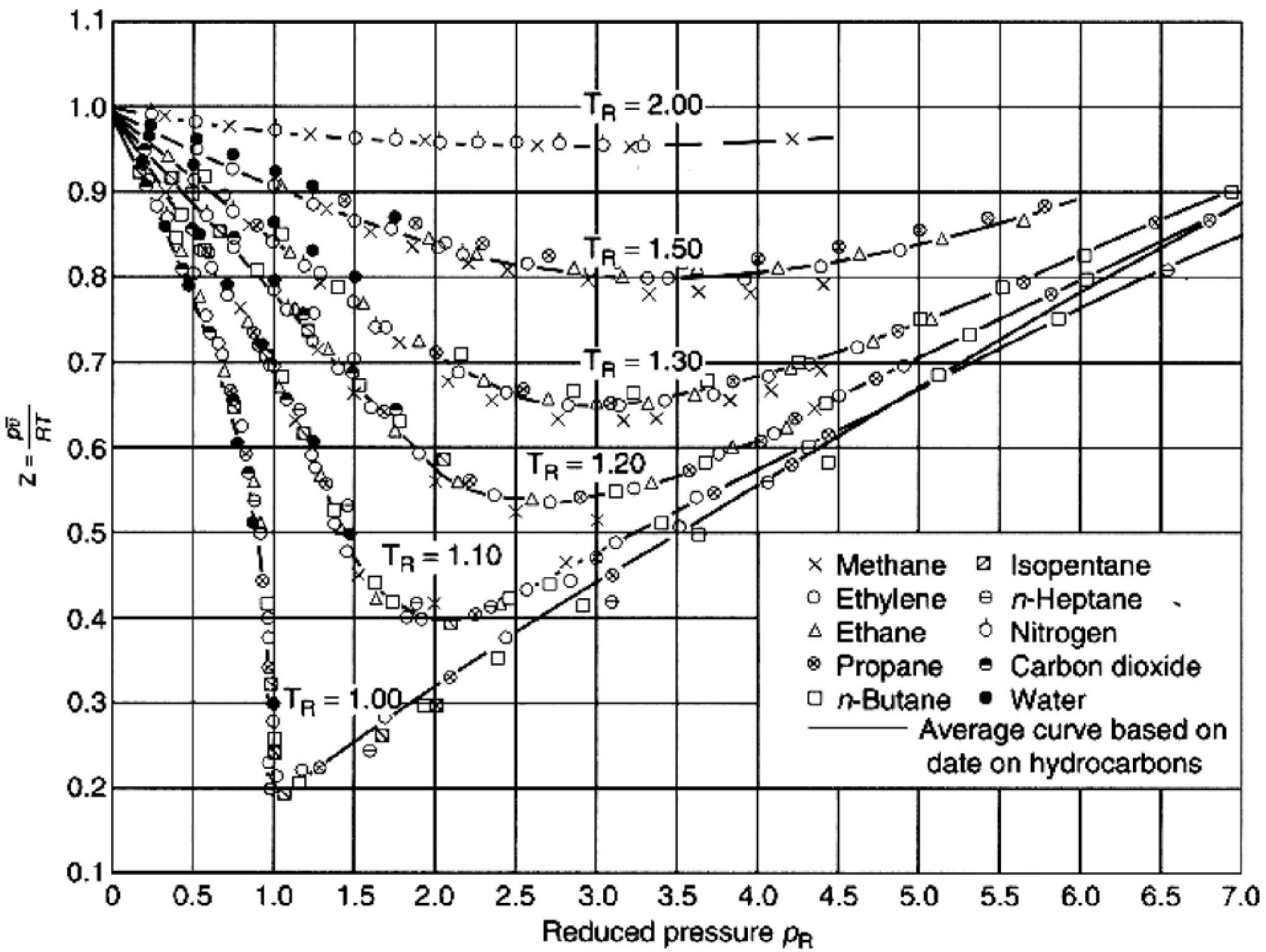

Figure 3.11 Generalized compressibility chart for various gases

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Examples of equations of state

- Ideal gas equation of state

$$Z = \frac{p\bar{v}}{\bar{R}T} = 1$$

- Virial equation of state (for non-ideal gasses)

$$Z = \frac{p\bar{v}}{\bar{R}T} = 1 + B(T)p + C(T)p^2 + D(T)p^3 + \ldots\ldots..$$

- Van der Waals equation of state (for non-ideal gasses)

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = n\bar{R}T$$

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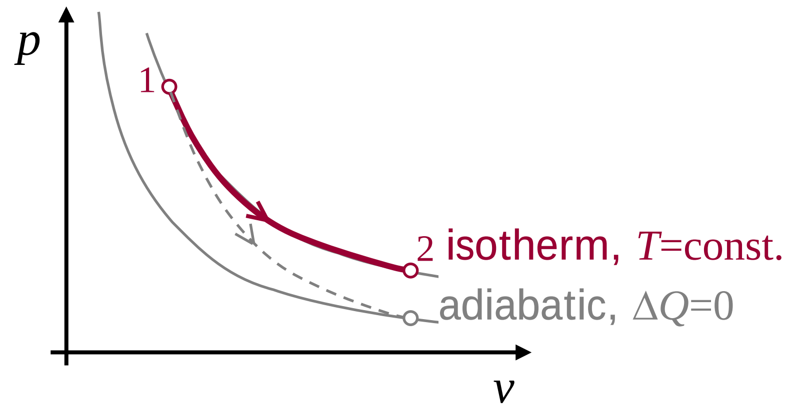
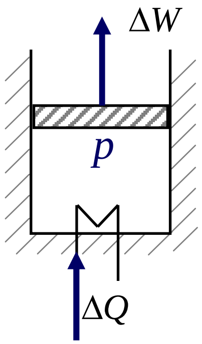
Isothermal expansion of an ideal gas





note: an isothermal process requires providing energy in form of heat during expansion, otherwise the temperature would decrease

first law $dU = \delta Q - \delta W$

$dU = 0$ because $u(T)$ and T=const.

$\delta W = pdV$

$p = \frac{n\bar{R}T}{V}$ ideal gas law

$$\Rightarrow \Delta_{12}Q = \Delta_{12}W = \int_{V_1}^{V_2} pdV = n\bar{R}T \int_{V_1}^{V_2} \frac{1}{V} dV = n\bar{R}T \ln \frac{V_2}{V_1}$$

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Adiabatic expansion of an ideal gas (c_v = constant)

$$du = \delta q - pdv = -pdv$$

$$c_v dT = -\frac{\overline{R}Tdv}{v}$$

$$c_v \frac{dT}{T} = -\overline{R}\frac{dv}{v}$$

$$c_v \int_{T_1}^{T_2} \frac{dT}{T} = -\overline{R}\int_{v_1}^{v_2} \frac{dv}{v}$$

$$c_v \ln\frac{T_2}{T_1} = -\overline{R}\ln\frac{v_2}{v_1}$$

after some math...

$$pv^{\kappa} = \text{constant (with } \kappa = \frac{c_p}{c_v}\text{)}$$

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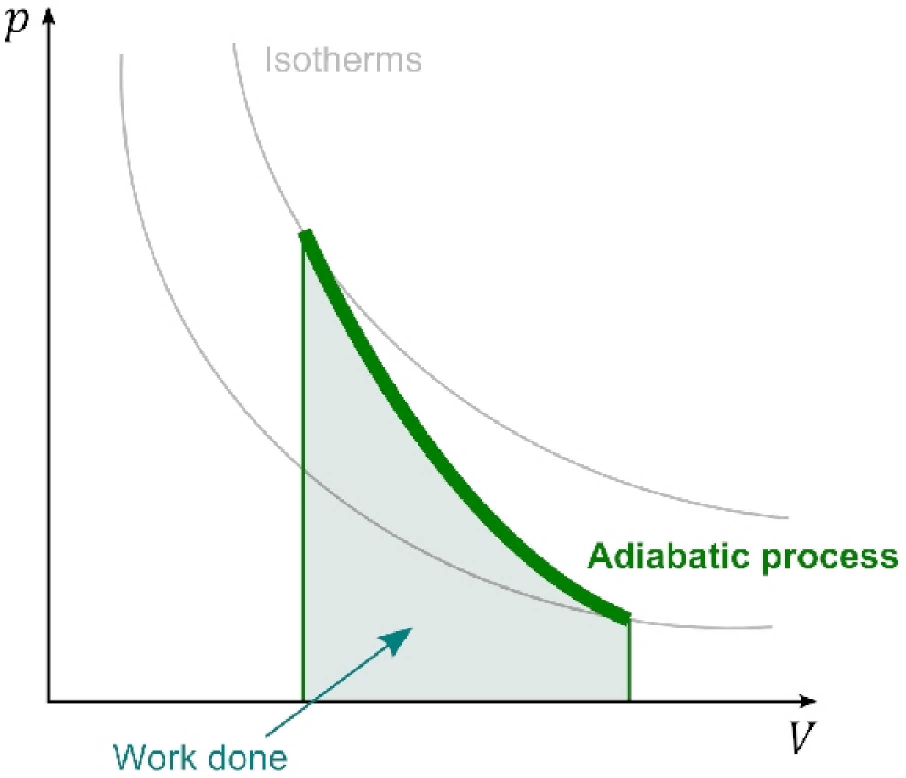
Adiabatic Expansion



$$pv^{\kappa} = \text{constant} \qquad \kappa = \frac{c_p}{c_v}$$

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Homework

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