

Thermodynamica 1

Bendiks Jan Boersma
Thijs Vlugt
Theo Woudstra

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college 10 – boek hoofdstuk 6

Thermodynamica 1

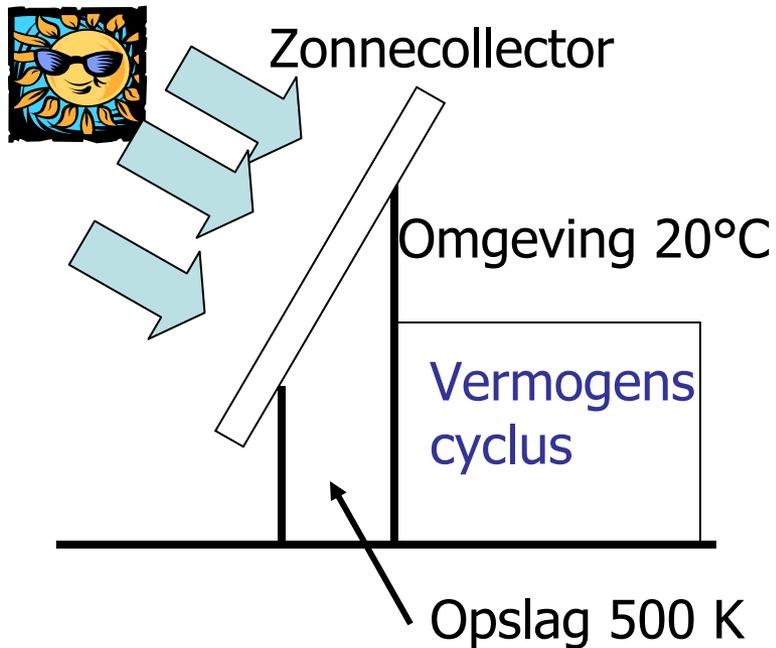
- Tweede hoofdwet
- Thermisch rendement
- Kelvin temperatuur schaal
- Carnot Kring proces → de ideale thermodynamische cyclus



Sadi Carnot

Concentrated solar power (CSP)

Voorbeeld: opgave 5.33



Concentrated Solar Power



Hot Salt

Molten salt can be used in solar-power generation to store heat until it is needed

Large mirrors focus the sun's rays on a central collection tower

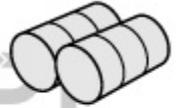


Molten salt is heated in the tower, then pumped into a storage tank



Cooled salt is returned to a second storage tank to be sent back through the cycle

The heated salt is then pumped through a steam generator



The steam is used to power an electric turbine

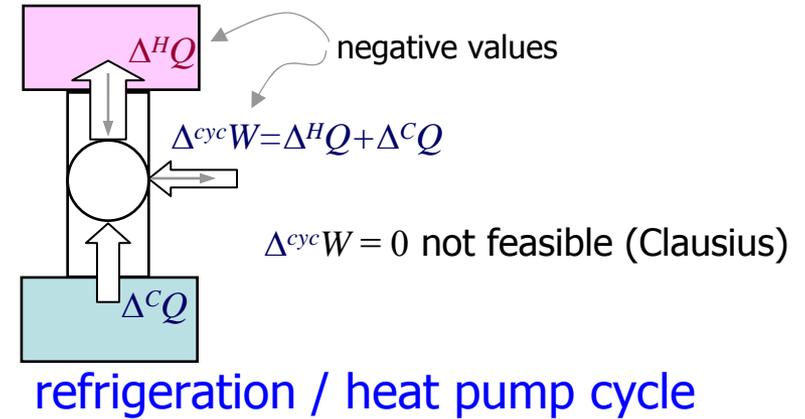
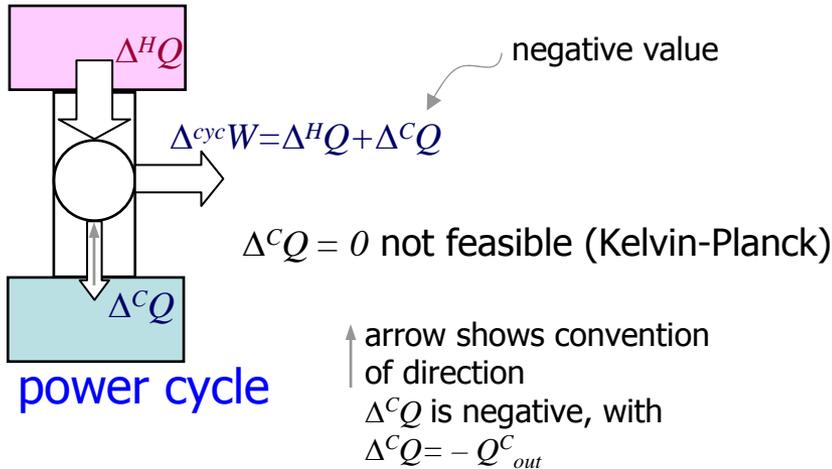


Source: United Technologies

Graphic by Eric Anderson



Recap: 2nd law and corollaries for cycle-processes



Analysis of (Carnot) power cycles revealed

- ⇒ even a **reversible** (i.e. idealized) power cycle has an efficiency of $\eta^{rev} < 1$
- ⇒ all **reversible Carnot-like** power cycles operating between the same temperature of two thermal reservoirs have the same thermal efficiency η^{rev}
 - irrespective of type of process-steps in power cycle processes
 - irrespective of working fluid

$$\eta^{Carnot} = \frac{\Delta^{cyc}W}{\Delta^H Q} = \underbrace{1 - \frac{|\Delta^C Q|}{\Delta^H Q}}_{\text{thermal efficiency } \eta^{th} \text{ of any power cycle}} = \underbrace{1 - \frac{T_C}{T_H}}_{\text{for Carnot cycle}}$$

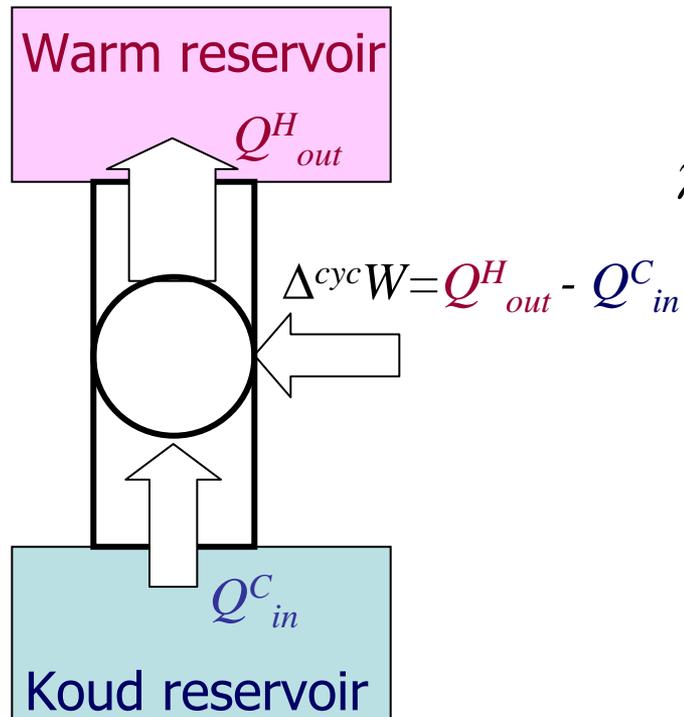
⇒ an **irreversible** (i.e. real) power cycle has yet a lower efficiency $\eta^{real} < \eta^{rev} < 1$

Koel- & Warmtepompkringprocessen

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Koel- & Warmtepompkringprocessen



Warmtepomp (WP) Warmtefactor (COP):

$$\gamma = COP_{WP} = \frac{Q_{out}^H}{\Delta^{cyc} W}$$

$$\gamma = \frac{Q_{out}^H}{Q_{out}^H - Q_{in}^C}$$

"coefficient of performance"

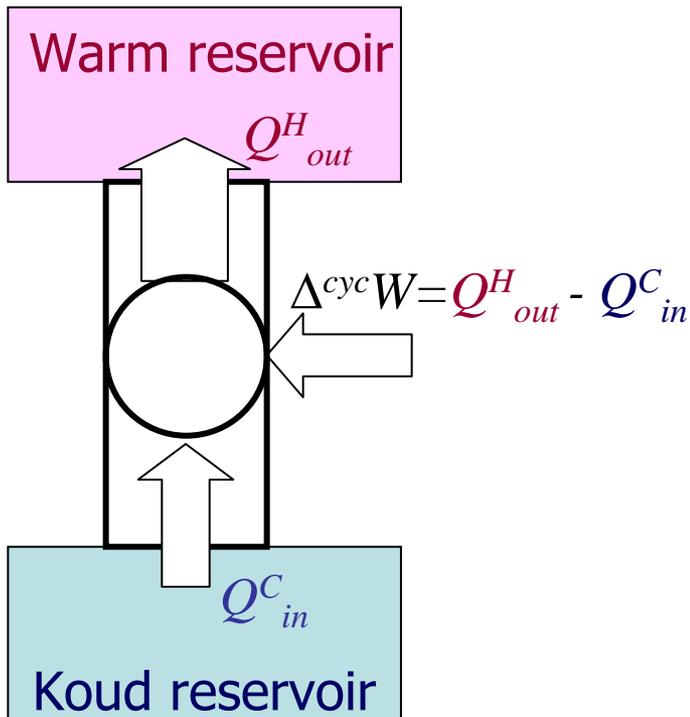
Koelmachine (KM) Koudefactor (COP):

$$\beta = COP_{KM} = \frac{Q_{in}^C}{\Delta^{cyc} W}$$

$$\beta = \frac{Q_{in}^C}{Q_{out}^H - Q_{in}^C}$$

- Hoewel het processchema voor koel- en warmtepompkringprocessen identiek is, verschillen de *COP's*
- $COP_{WP} \geq 1$ Uit de definitie volgt: $\gamma = \beta + 1$
- Een reversibel kringproces heeft de hoogst mogelijke waarde van *COP*

Maximum rendement van koel- & WP-kringprocessen



voor Carnot-proces

$$\left(\frac{Q_{in}^C}{Q_{out}^H} \right)_{Carnot} = \frac{T_C}{T_H}$$

Warmtepomp (WP) Warmtefactor (COP)

$$COP_{WP} = \frac{Q_{out}^H}{Q_{out}^H - Q_{in}^C}$$

$$COP_{WP, Carnot} = \frac{T_H}{T_H - T_C}$$

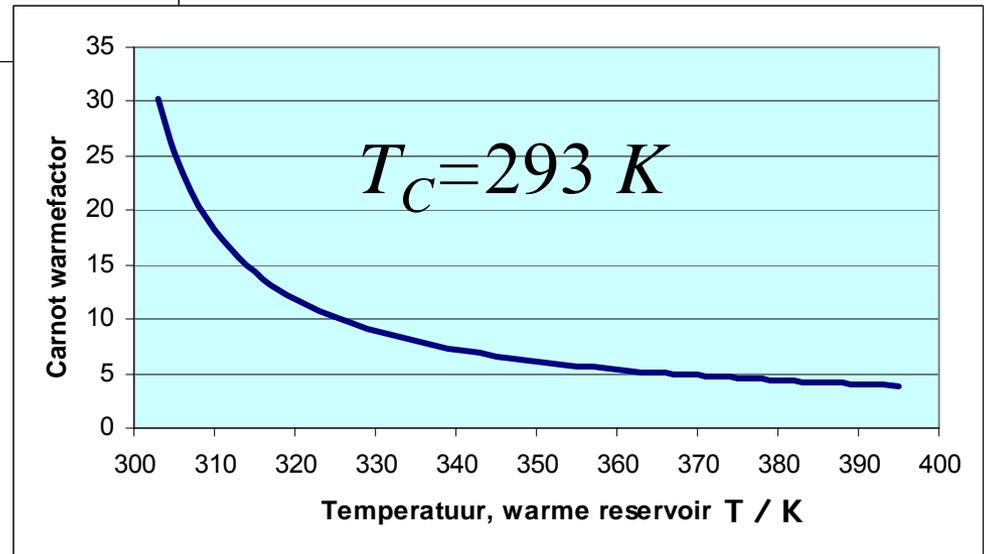
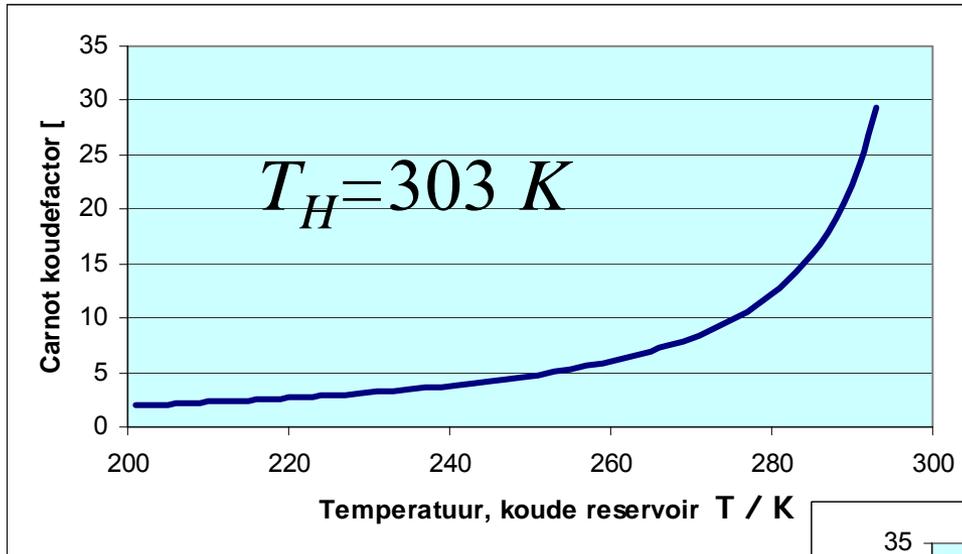
Koelmachine (KM) Koudefactor (COP)

$$COP_{KM} = \frac{Q_{in}^C}{Q_{out}^H - Q_{in}^C}$$

$$COP_{KM, Carnot} = \frac{T_C}{T_H - T_C}$$

Het maximale rendement vereist een proces met isotherme warmteoverdracht ("Carnot-like" proces)

Maximum rendement van koel- & WP-kringprocessen



Voorbeeld 1

De omgeving van een vrieskast heeft een temperatuur van 27°C . Om de vrieskast op -40°C te houden moet een energiestroom van 1.25 kW afgevoerd worden

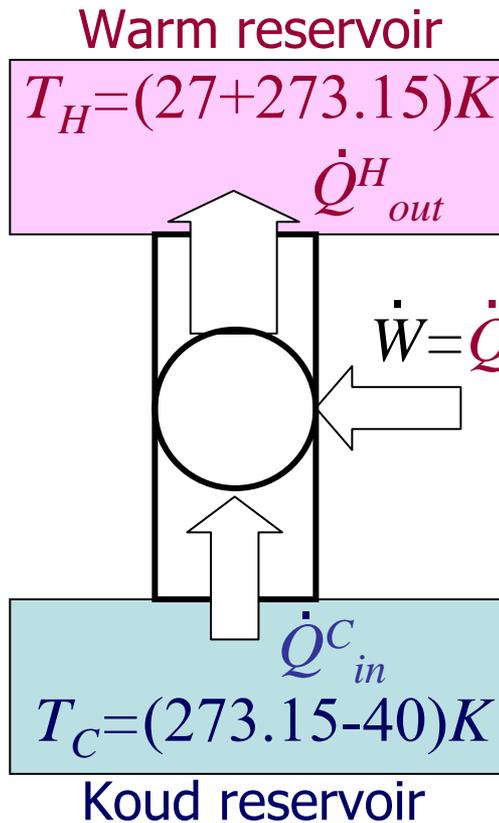
Bepaal

- (1) De maximale koudefactor (COP).
- (2) Het minimum theoretisch gevraagd aandrijfvermogen, in kW , voor een koelkringproces dat onder deze omstandigheden werkt

$$COP = 3.5$$

$$W = 0.35 \text{ kW}$$

Voorbeeld 1 (uitwerking)



$$COP_{koelmachine} = \frac{T_C}{T_H - T_C} = \frac{233.15K}{67.0K} = 3.48$$

$$COP_{koelmachine} = \frac{\dot{Q}_{in}^C}{\dot{Q}_{out}^H - \dot{Q}_{in}^C}$$

$$\dot{W} = \dot{Q}_{out}^H - \dot{Q}_{in}^C = \frac{\dot{Q}_{in}^C}{COP_{koelmachine}} = \frac{1.25kW}{3.48} = 0.359kW$$

Warmtepomp of CV ketel

- CV ketel op gas ongeveer 25 kW
- Rendement 95%
- Stookwaarde gas 32MJ/m³
- Verbruik /h = 2.7 m³ = (2 Euro)

- Warmtepomp 25 kW
- $T_h = 22$ graden celsius, $Q_h = 25$ kW
- $T_l = 4$ graden celsius $Q_l = 23.5$ kW
- Theoretische arbeid $W = 1.5$ kW (COP = 16)
- Rendement 25% Benodigd vermogen 6.0kW (COP = 16 * .25 = 4)
- Verbruik/h = 6kWh = (1.5 Euro)

- Aanschafprijs warmtepomp is hoger, een COP van 4 is realiseerbaar
- Warmtepomp neemt meer ruimte in
- $T_l = 15$ graden celsius → 0.56 Euro



Aardwarmte



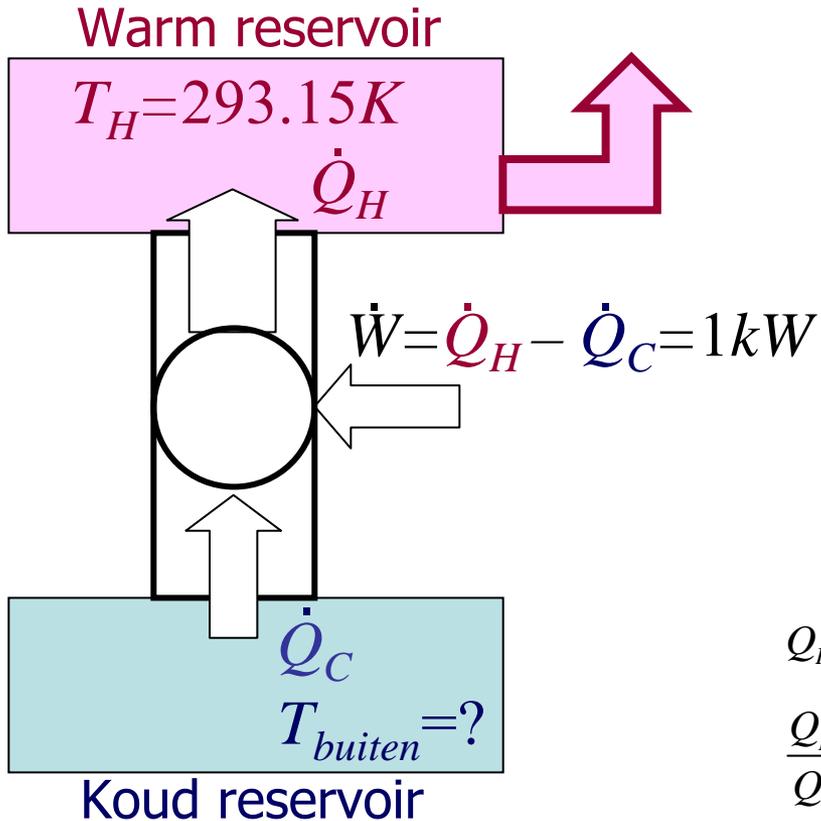
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Voorbeeld 2

- Een ideale Carnot-warmtepomp heeft een aandrijfvermogen van 1 kW nodig om een woning op 20°C te houden
- Het warmtetransport door wanden en dak is gelijk aan 3000 kJ/h per graad temperatuurverschil tussen binnen en buiten (warmtebron)
- Bepaal de laagste buitentemperatuur waarvoor de warmtepomp nog voldoet
- Opmerking: deze buitentemperatuur is ook de temperatuur van het koude reservoir

Voorbeeld2 (uitwerking)



$$T_H = 20^\circ C$$

$$W = -1 kW$$

$$\left. \begin{aligned} Q_H &= \frac{3000}{3600} (T_H - T_L) \\ \frac{Q_H}{Q_L} &= \frac{T_H}{T_L} \\ Q_H &= Q_L + W \end{aligned} \right\} Q_H \left(1 - \frac{T_H}{T_L} \right) = W \Rightarrow Q_H = W \left(1 - \frac{T_H}{T_L} \right)^{-1}$$

$$W \left(1 - \frac{T_H}{T_L} \right)^{-1} = \frac{3000}{3600} (T_H - T_L) \Rightarrow -1 \left(1 - \frac{293}{T_L} \right)^{-1} = \frac{3}{3.6} (293 - T_L)$$

$$T_L \approx 275 K$$

Entropy

& the 2nd law as a balance equation

Analyzing the Carnot power cycle – the entropy

- From the 1st and 2nd law we know that

$$\eta^{rev} = 1 - \frac{|\Delta^C Q|}{\Delta^H Q} = 1 - \frac{T^C}{T^H}$$

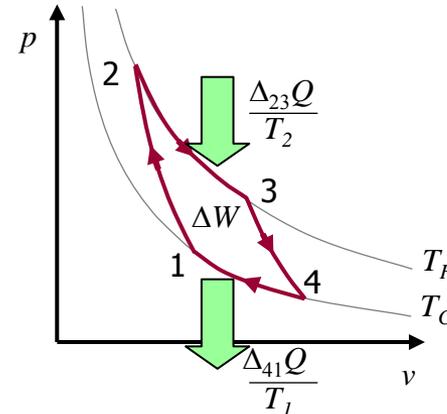
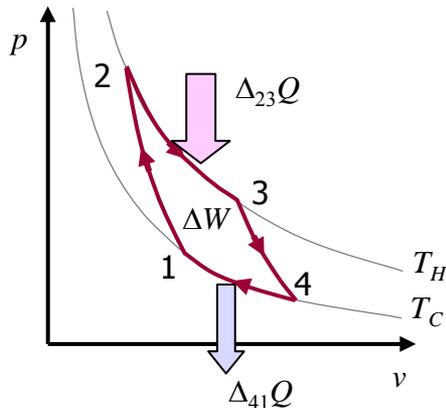
Carnot

$\Delta^C Q = -Q_{out}^C$ negative value according to regular convention (ΔQ in the direction of system)

- from

$$\frac{|\Delta^C Q|}{\Delta^H Q} = \frac{T^C}{T^H} \Rightarrow \frac{|\Delta^C Q|}{T^C} = \frac{\Delta^H Q}{T^H} \Rightarrow \frac{\Delta^C Q}{T^C} + \frac{\Delta^H Q}{T^H} = 0$$

- it's clear, that the sum of the ratio $\Delta Q/T$ is preserved in a **reversible** Carnot cycle



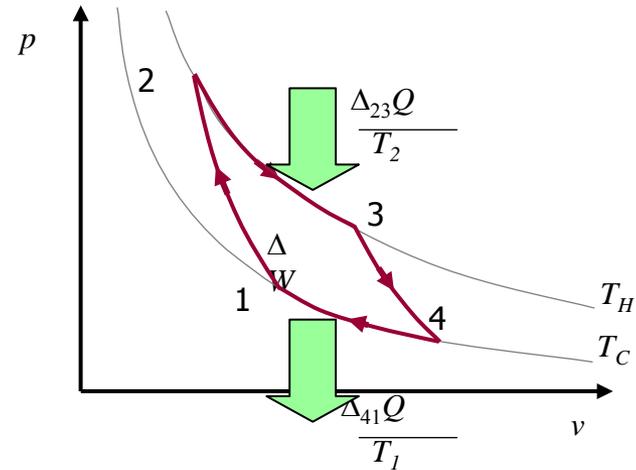
$\Delta Q/T$ passes unchanged through reversible cycles

Toelichting

$$\Delta_{23}Q = mRT_H \ln(V_3 / V_2)$$

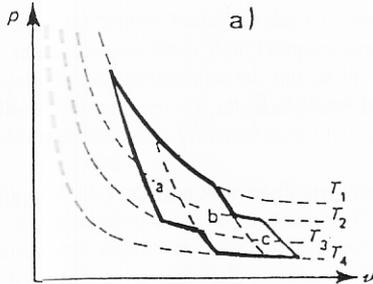
$$\Delta_{14}Q = mRT_C \ln(V_4 / V_1)$$

$$V_3 / V_2 = V_4 / V_1 \Rightarrow \frac{\Delta_{23}Q}{T_H} = \frac{\Delta_{14}Q}{T_C}$$



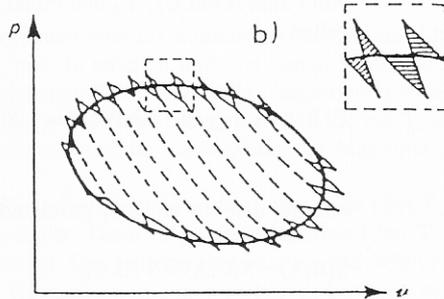
Generalizing to arbitrary reversible cycles – the entropy

- We can consider a reversible cycle with multiple Carnot-steps (i.e. multiple adiabatic and isothermal steps)



analysis of such cycles gives $\Rightarrow \sum_i \frac{\Delta^i Q}{T^i} = 0$ (#)

- We can then consider arbitrary reversible cycles. We can always substitute them by an equivalent cycle composed of infinitesimal Carnot-steps



from (#) with $\Delta \rightarrow 0 \Rightarrow \oint \frac{\delta Q}{T} = 0$

\Rightarrow the ratio $\Delta Q/T$ (or $\delta Q/T$) is preserved in any **reversible** cycle. Clausius called this ratio the **entropy S** , with

$$dS = \frac{\delta Q}{T} \quad \text{unit of entropy } S \text{ is [J/K]} \quad \text{and} \quad \oint dS = \oint \frac{\delta Q}{T} = 0$$

2nd law for reversible processes in closed system

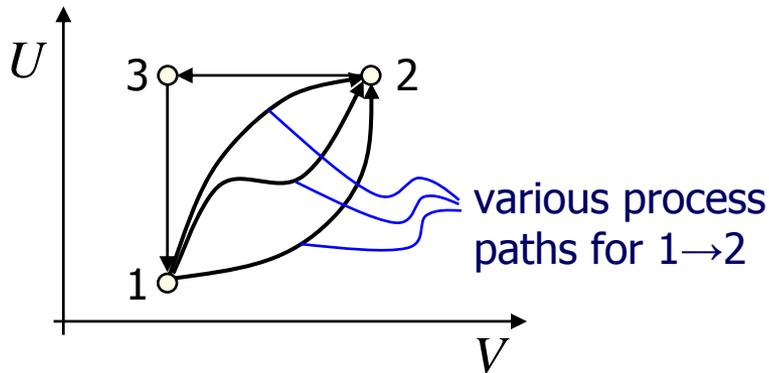
The entropy – a state property (toestandsgrootheid)

With the first law $dU = \delta Q - pdV$

we can rewrite $\oint dS = \oint \frac{\delta Q}{T} = 0$

as $\oint dS = \oint \frac{1}{T}(dU + pdV) = 0$

We analyze an arbitrary cycle process $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$



$$\oint dS = \int_1^2 dS + \int_2^3 dS + \int_3^1 dS = 0$$

since this equation holds for any process path $1 \rightarrow 2$, we conclude that $\int dS$ is **not path-dependent** \Rightarrow

$$\int_1^2 dS = S_2 - S_1 = S(T_2, v_2) - S(T_1, v_1)$$

\Rightarrow the entropy is a **state property**. It is fully determined at a thermodynamic state point, say (T, v) (or for mixtures (T, v, x_i)).

The entropy - variables

Like for any other state property, the entropy S is fully defined, for a set of variables that fully specify a state, such combinations can be $S(v,T)$, $S(p,T)$, $S(p,v)$, $S(h,T)$, ... (for pure components, otherwise the composition x_i also needs to be specified)

Often times, the entropy is expressed as $S(v,T)$, or $S(p,T)$

The second law of Thermodynamics

- one can write the 2nd law for closed systems in differential & in integral form

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

$$\Delta_{12}S = \int_1^2 \frac{\delta Q}{T} + \underbrace{\int_1^2 \delta\sigma}_{\Delta_{12}\sigma} \quad \Delta_{12}\sigma \geq 0 \quad (\text{closed system})$$

$\delta\sigma = 0, \quad \Delta_{12}\sigma = 0$ **entropy production** for reversible processes

$\delta\sigma > 0, \quad \Delta_{12}\sigma > 0$ **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)

Cycle process with irreversibilities

Let's compare a Carnot cycle with a "Carnot-like" cycle where irreversibilities prevail. Both cycles will have the same heat transfer $\Delta^H Q$ from the warm reservoir

The first law for the Carnot cycle

$$\Delta W^{Carnot} = \Delta^H Q + \Delta^C Q^{Carnot} \quad (1)$$

& "Carnot-like" cycle with irreversibilities

$$\Delta W^{irrev} = \Delta^H Q + \Delta^C Q^{irrev} \quad (2)$$

The second law for a Carnot cycle, is

$$\frac{\Delta^C Q^{Carnot}}{T^C} + \frac{\Delta^H Q}{T^H} = 0 \quad (3)$$

& for the irreversible cycle, it is

$$\frac{\Delta^C Q^{irrev}}{T^C} + \frac{\Delta^H Q}{T^H} + \Delta^{cyc} \sigma = 0 \quad (4)$$

$$(2) \text{ in } (1) \quad \Delta W^{Carnot} - \Delta W^{irrev} = \Delta^C Q^{Carnot} - \Delta^C Q^{irrev}$$

$$(2) \text{ in } (1) \quad \Delta^C Q^{Carnot} - \Delta^C Q^{irrev} = T_C \sigma^{cyc}$$

⇒

$$\Delta W^{Carnot} - \Delta W^{irrev} = T_C \cdot \Delta^{cyc} \sigma \quad \text{and} \quad \eta^{irrev} = \eta^{Carnot} \cdot \eta_\sigma \quad \text{with}$$

$$\eta_\sigma = \frac{\Delta W^{irrev}}{\Delta W^{Carnot}} = 1 - \frac{T_C \cdot \Delta^{cyc} \sigma}{\Delta W^{Carnot}}$$

⇒ the **entropy production** (times a reference temperature) is the "**lost work**" (i.e. non-utilized work potential) due to irreversibilities.

The third law of Thermodynamics

- the entropy of matter at $T=0K$ is zero independent of pressure or the type of crystalline phase

$$S(T = 0K, P) = S(T = 0K) = 0 J/K$$

- The third law is no definition, but a finding
- It was determined experimentally (Nernst) and supplemented theoretically by Statistical Thermodynamics (Planck)

the temperature $T=0K$ can not be reached experimentally, however. In fact that is a result of the 2nd law saying: the efficiency of a refrigeration system approaches zero when T_C approaches zero

Working with the entropy and the 2nd law

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Combining the 1st and 2nd law – the $T \cdot dS$ equations

The first law for closed systems reads

$$dU = \underbrace{\delta Q_{int.rev}}_{= TdS \text{ (2nd law)}} - \underbrace{\delta W_{int.rev}}_{= pdV}$$

⇒ $dU = TdS - pdV$ the Gibbs equation (for pure components)

with $H = U + pV$ ⇒ $dH = dU + d(pV)$
 $= dU + pdV + Vdp$

⇒ $dH = TdS + Vdp$

the equations follow from considering a closed system. But they relate only state properties of the involved **material**. It does not matter if the material is in an open or closed system and the equations are not restricted to closed systems.

these equations are not applied to process steps, they relate material properties. Molecular motion of materials is perpedual (reversible), so that the assumption "int.rev." is justified!

Entropy change of an ideal gas

For an ideal gas, $u(T,V)$ and $h(T,P)$ are functions of T only; $u(T)$ and $h(T)$

$$\Rightarrow \quad du = c_v^{ig} dT \quad \text{and} \quad c_v^{ig} = c_v^{ig}(T)$$

$$\Rightarrow \quad dh = c_p^{ig} dT \quad \text{and} \quad c_p^{ig} = c_p^{ig}(T)$$

and $Pv = RT$

$$du = Tds - pdv \quad \Rightarrow \quad ds = \frac{du}{T} + \frac{p}{T} dv$$

$\underbrace{\quad}_{= R/v} \quad \text{(ideal gas)}$

$$\Rightarrow \quad ds = \frac{c_v^{ig}(T)}{T} dT + R \cdot d \ln(v)$$

$$\Rightarrow \quad s(T_2, v_2) - s(T_1, v_1) = \int_{T_1}^{T_2} \frac{c_v^{ig}(T)}{T} dT + R \cdot \ln \left(\frac{v_2}{v_1} \right)$$

Entropy change of an ideal gas

For an ideal gas, $u(T,V)$ and $h(T,P)$ are functions of T only; $u(T)$ and $h(T)$

$$\Rightarrow \quad du = c_v^{ig} dT \quad \text{and} \quad c_v^{ig} = c_v^{ig}(T)$$

$$\Rightarrow \quad dh = c_p^{ig} dT \quad \text{and} \quad c_p^{ig} = c_p^{ig}(T)$$

$$\text{and} \quad Pv = RT$$

$$dh = Tds + vdp \quad \Rightarrow \quad ds = \frac{dh}{T} - \frac{v}{T} dp$$

$\underbrace{\quad}_{=R/p} \quad (\text{ideal gas})$

$$\Rightarrow \quad ds = \frac{c_p^{ig}(T)}{T} dT - R \cdot d \ln(p)$$

$$\Rightarrow \quad s(T_2, p_2) - s(T_1, p_1) = \int_{T_1}^{T_2} \frac{c_p^{ig}(T)}{T} dT - R \cdot \ln\left(\frac{p_2}{p_1}\right)$$

Voorbeeld: opgave 6.33

- Lucht wordt gecomprimeerd van een toestand met druk 0.1 MPa en temperatuur 27°C naar een toestand met druk 0.5 MPa en temperatuur 177 °C
- Kan dit proces adiabatisch verlopen?
- In geval het antwoord positief is, bereken de arbeid per kg lucht, in kJ/kg
Anders, bepaal de richting van de warmteoverdracht

$$s(T_2, p_2) - s(T_1, p_1) = s^\circ(T_2) - s^\circ(T_1) - R \ln \frac{p_2}{p_1}$$

$$T_1 = 300.15 K \quad \text{Tabel_A22} \Rightarrow s^\circ(T_1 = 300.15 K) = 1.70253 \frac{\text{kJ}}{\text{kg K}}$$

$$T_2 = 450.15 K \quad \text{Tabel_A22} \Rightarrow s^\circ(T_2 = 450.15 K) = 2.11195 \frac{\text{kJ}}{\text{kg K}}$$

$$s(T_2, p_2) - s(T_1, p_1) = (2.11195 - 1.70253) \frac{\text{kJ}}{\text{kg K}} - \frac{8.314 \frac{\text{kJ}}{\text{kmol K}}}{28.97 \frac{\text{kg}}{\text{kmol}}} \ln \left(\frac{0.5 \text{ MPa}}{0.1 \text{ MPa}} \right)$$

$$= -0.05247 \frac{\text{kJ}}{\text{kg K}}$$

Er wordt warmte afgevoerd

Waarom?

Entropy of incompressible liquids & solids

$$du = Tds - pdv \quad \Rightarrow \quad ds = \frac{du}{T} + \frac{p}{T} \cancel{dv} \quad \underbrace{\hspace{1cm}}_{=0}$$

$$du = \left(\frac{\partial u}{\partial T} \right)_v dT + \left(\frac{\partial u}{\partial v} \right)_T \cancel{dv} \quad \Rightarrow \quad du \cong c_p(T) dT$$

$$\underbrace{\hspace{1cm}}_{= c_v(T, v) = c_v(T) \cong c_p(T)}$$

incompressible

$$\Rightarrow ds = \frac{c_p(T)}{T} dT$$

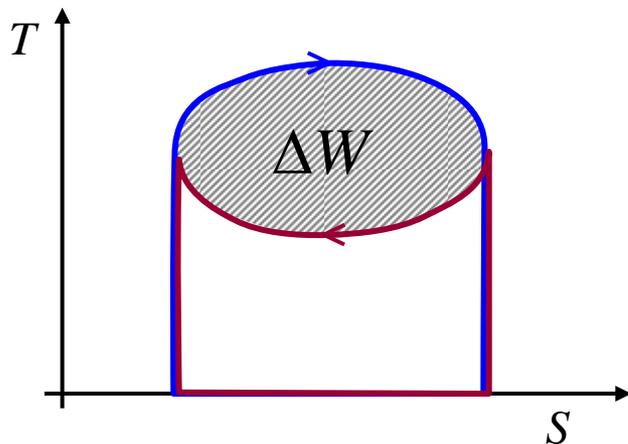
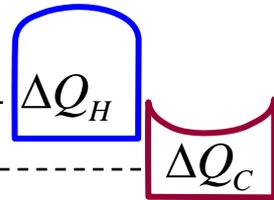
$$\Rightarrow s(T_2, p_2) - s(T_1, p_1) = \int_{T_1}^{T_2} \frac{c_p}{T} dT$$

$$\Rightarrow s(T_2, p_2) - s(T_1, p_1) = s^0(T_2) - s^0(T_1)$$

where $\{p_1, p_2\}$ is within the range, where substance is assumed incompressible

T-S Diagram

- we have seen, that the entropy is a state variable – a given state-point (T, V) or (T, P) or (P, V) for pure components one-to-one defines the entropy S at this state
- the entropy can be calculated from the Gibbs equation
- Given this, reversible cycle processes can be evaluated in T - S diagrams. The advantage of such diagrams are
 - that $\Delta Q_H = \int TdS$ holds for the upper part of a cycle process
 - and $\Delta Q_C = \int TdS$ holds for the lower part of a cycle process
 - the work of the cycle is obtained from $\Delta W = \Delta Q_H - |\Delta Q_C|$
 - an adiabatic reversible process is, because of $\delta Q = TdS = 0 \text{ kJ}$ an isentropic process and is represented as a vertical line

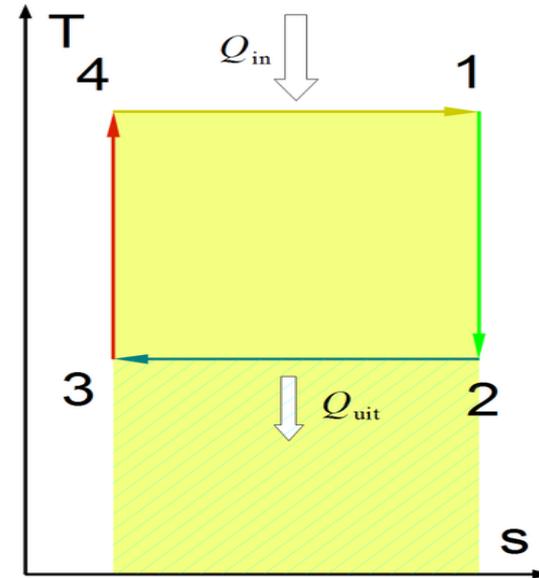
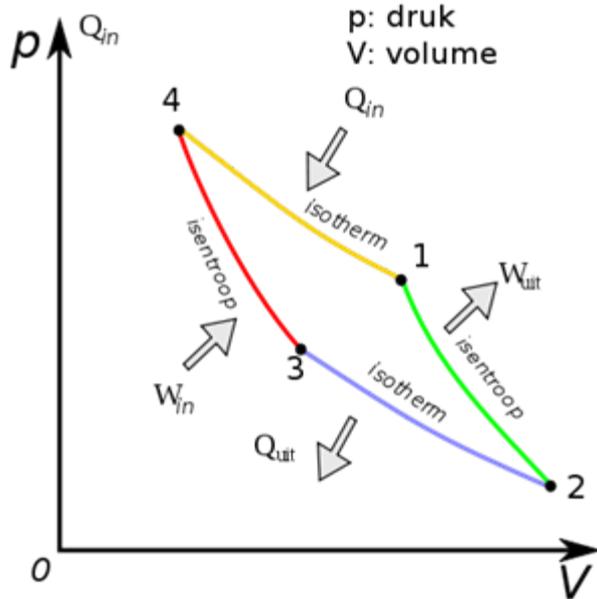


T-S versus P-V diagram

- Arbeidsdiagram p versus V
- Warmtediagram T versus S

$$\delta W = p dV$$

$$\delta Q = T dS$$



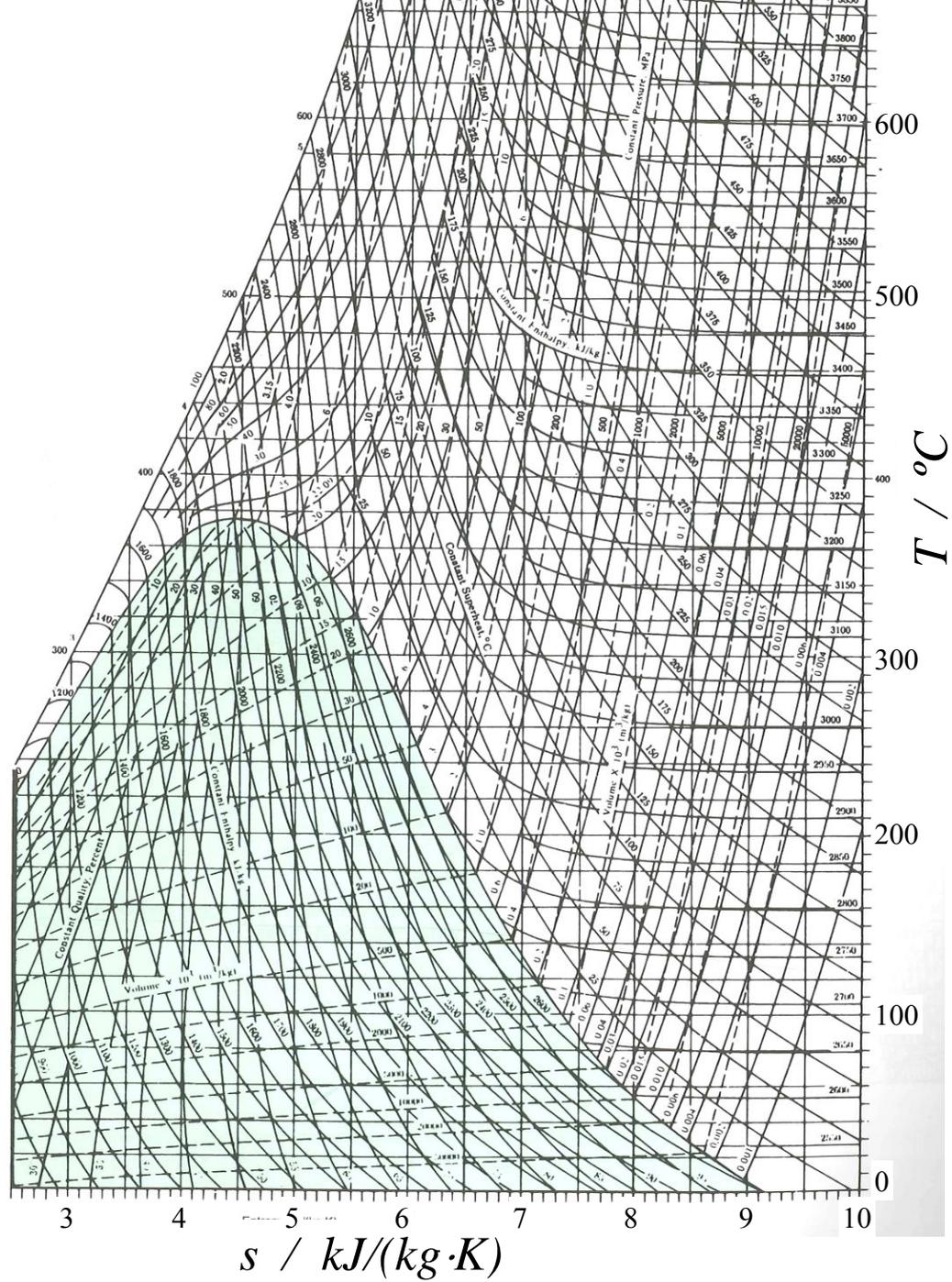
Adiabatisch reversibel proces is isentroop, dus $S = \text{constant}$

Oppervlakken zijn precies even groot omdat

$$Q_{cyc} = W_{cyc}$$

$$\int T dS = \int p dV$$

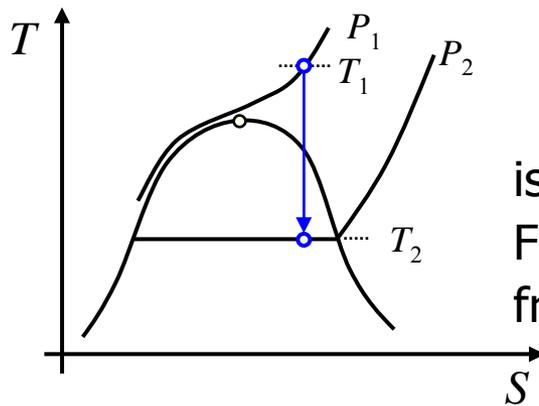
T-S Diagram



Adiabatic reversible processes \Rightarrow Isentropic processes

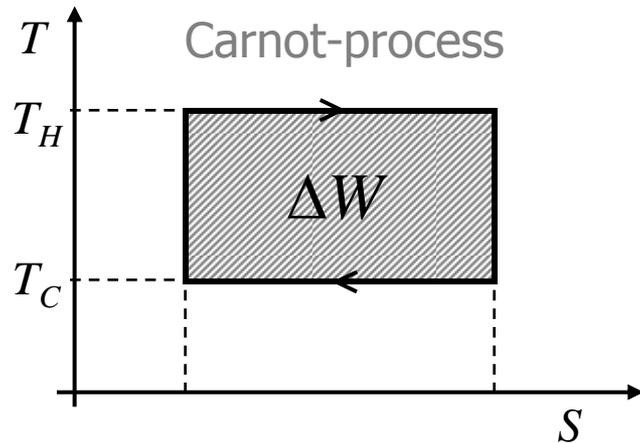
- isentropic = 'with constant entropy S '

- second law for adiabatic reversible processes $dS = \underbrace{\frac{\delta Q}{T}}_{=0} + \underbrace{\delta\phi}_{=0} \Rightarrow S = \text{const.}$
- adiabatic reversible



isentropic expansion from pressure p_1 to p_2 .
 From T - s -diagram, one obtains T_2 and vapor fraction x^{vap} ("quality") $s = (1 - x^{vap})s_f + x^{vap}s_g$

Carnot process in a T - S diagram



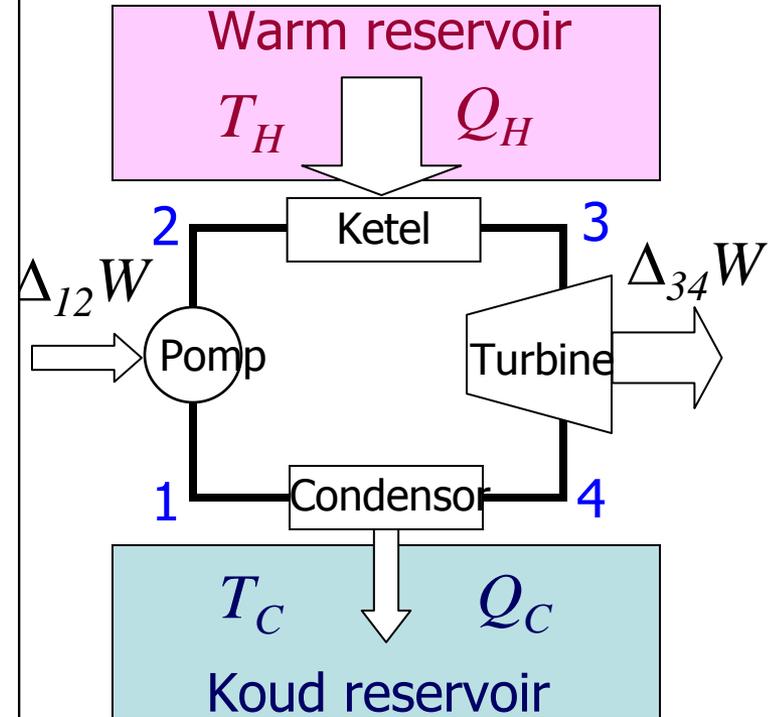
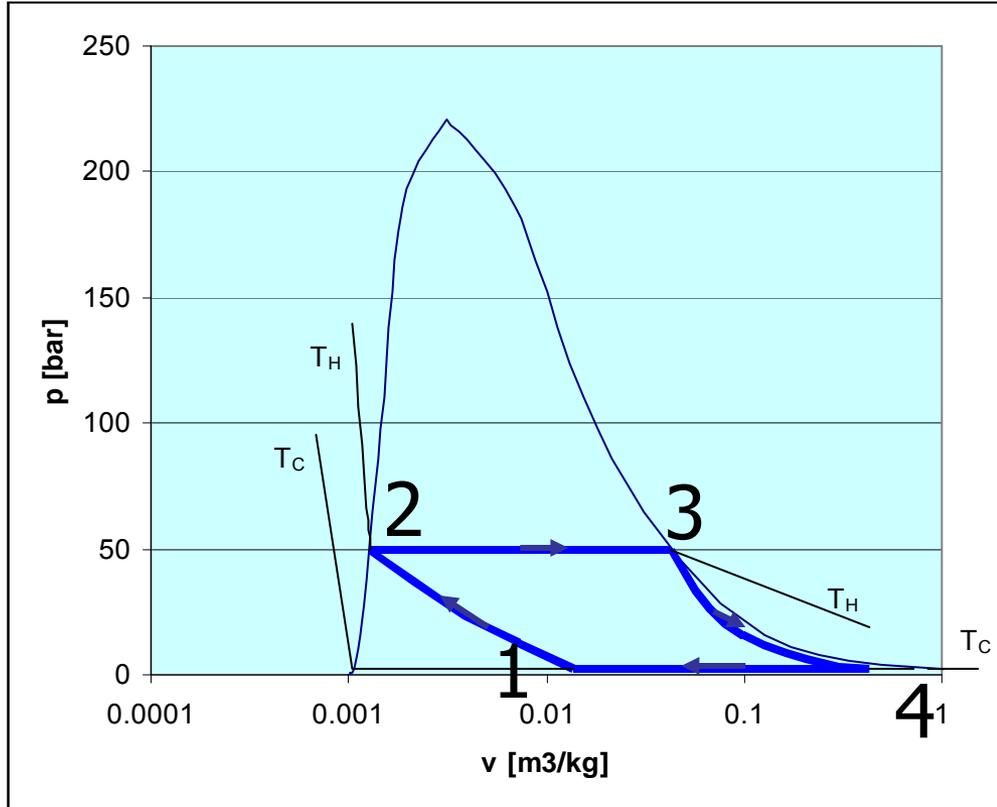
The Carnot process is composed of 2 isothermal and 2 adiabatic process steps

In a T - S diagram they are represented by two horizontal and 2 vertical process steps, respectively

It is graphically clear, that for a given T_H and given T_C , no cycle process can have a higher thermal efficiency than the Carnot process

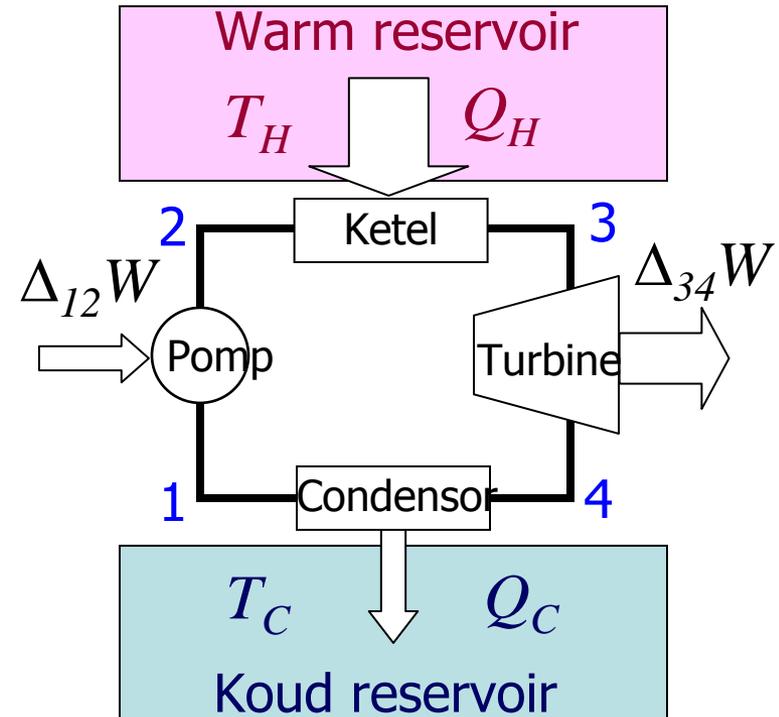
Two other cycle processes will turn out to also have the Carnot efficiency – both, of course, have 2 isothermal process steps

Carnot waterdamp-vermogenskringproces



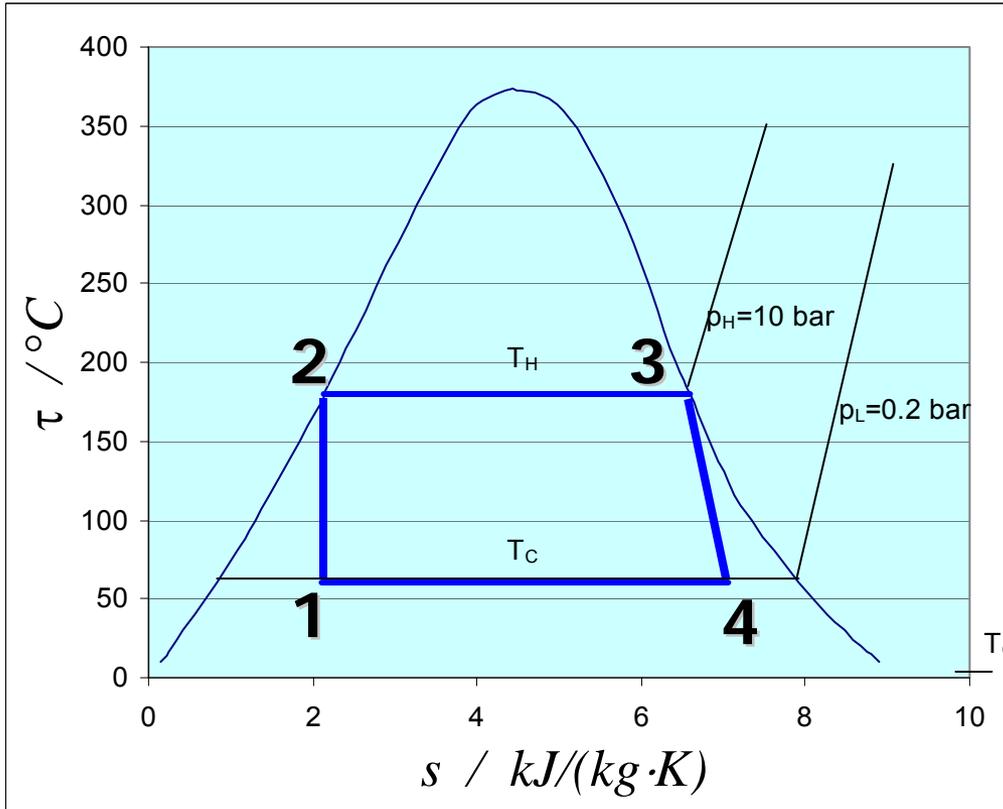
Voorbeeld: opgave 6.24

- De figuur is een schema van een waterdamp vermogenskringproces waarin water door de vier componenten stroomt. Het water stroomt door ketel en condensor met constante druk en stroomt adiabatisch door turbine en pomp.
- Schets het kringproces in een T - s diagram.;
- Bepaal het thermisch rendement van een Carnot vermogenskringproces dat tussen dezelfde minimum en maximum temperaturen opereert.



2 verzadigd vloeistof met 10 bar
3 verzadigd damp met 10 bar
4 $x=88\%$; 0.2 bar
1 $x=18\%$; 0.2 bar.

Voorbeeld: opgave 6.24



Tabel A-3

- 2 $\tau=179.9^{\circ}\text{C}$; $s=2.1387 \text{ kJ/kgK}$
 3 $\tau=179.9^{\circ}\text{C}$; $s=6.5863 \text{ kJ/kgK}$
 4 $\tau=60.06^{\circ}\text{C}$;
 $s=(0.88*7.9085 + (1-0.88)*$
 $0.8320) \text{ kJ/kgK} = 7.059 \text{ kJ/kgK}$
 1 $\tau=60.06^{\circ}\text{C}$;
 $s=(0.18*7.9085 + (1-0.18)*$
 $0.8320) \text{ kJ/kgK} = 2.106 \text{ kJ/kgK}$

$$\eta_{Carnot} = 1 - \frac{T_C}{T_H} = 1 - \frac{60.06 + 273}{179.9 + 273} = 0.27$$

$$\frac{Q_C}{Q_H} = \frac{T_H \Delta S}{T_C \Delta S} = .$$

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Aanwijzingen voor zelfstudie

- H6.1 – 6.4 en 6.5.1 – 6.5.4 zijn behandeld. Goed doorlezen.
- Maak opgaven 6.1, 6.7, 6.9
- Maak enkele van de opgaven 6.18 – 6.25
- Maak opgave 6.28, 6.29, 6.35 en 6.30 + 6.31 (er is een tikfout in opgave 6.31, bedoeld is ... reconsider the data of problem 6.30...)
- Maak opgaven 6.38