

# Kretsprosesser. 2. hovedsetning

Reversible og irreversible prosesser (20.1)

Adiabatisk prosess (19.8)

Kretsprosesser:

varmekraftmaskiner (20.2+3)

kjølemaskiner (20.4)

I dag

Carnotsyklusen (20.6)

Eks: Ottosyklus (20.3)

2. hovedsetning (20.5)

Carnots teorem og Carnots (u)likhet

Entropi (20.7)

Entropien mikroskopisk forklart (20.8)

**Kretsprosess:** Start = Slutt

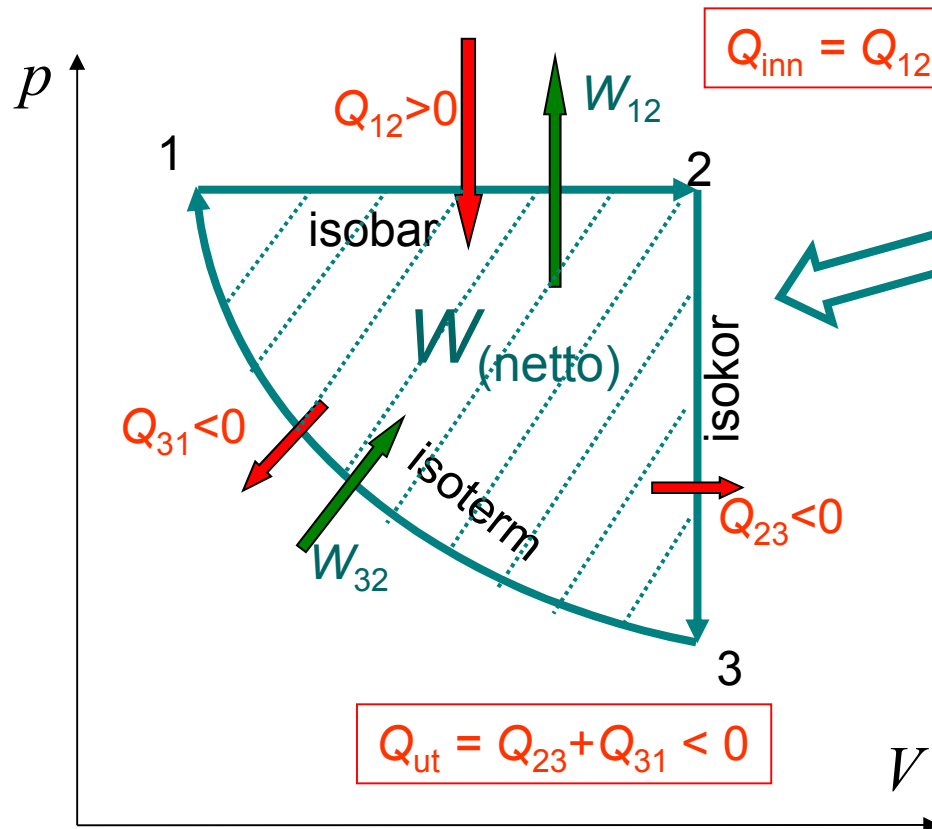
**REPETISJON**

$$U_1 = U_1$$

$$\Delta U = 0$$

$$Q_{(\text{netto})} = W_{(\text{netto})}$$

**Eks. 1:**



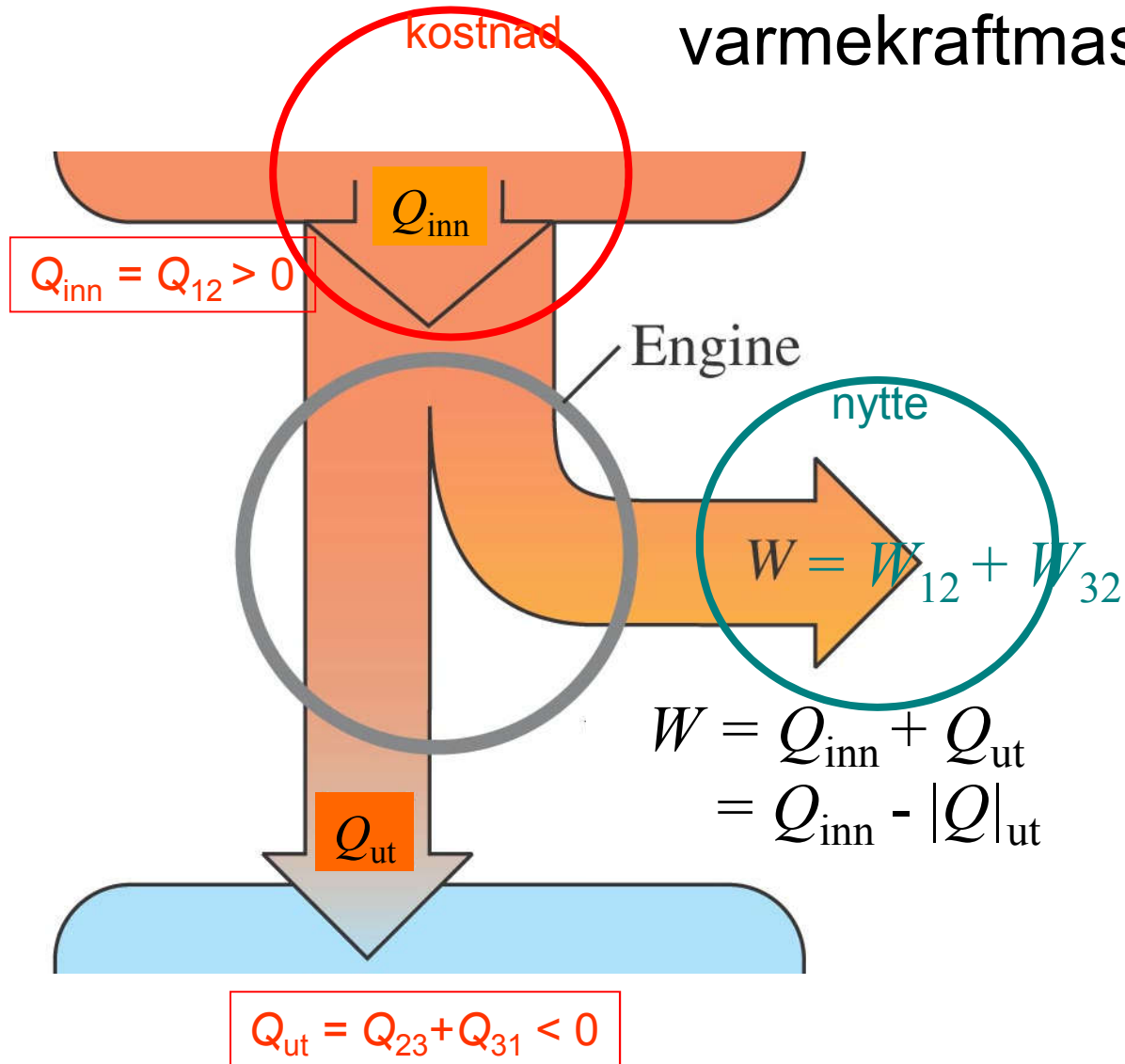
**Varmekraftmaskin**

varme:  $Q_{(\text{netto})} > 0$   
arbeid:  $W_{(\text{netto})} > 0$  (ut)

**Kjølemaskin**

arbeid:  $W_{(\text{netto})} < 0$  (inn)  
varme:  $Q_{(\text{netto})} < 0$

# Energifyttdiagram for varmekraftmaskin

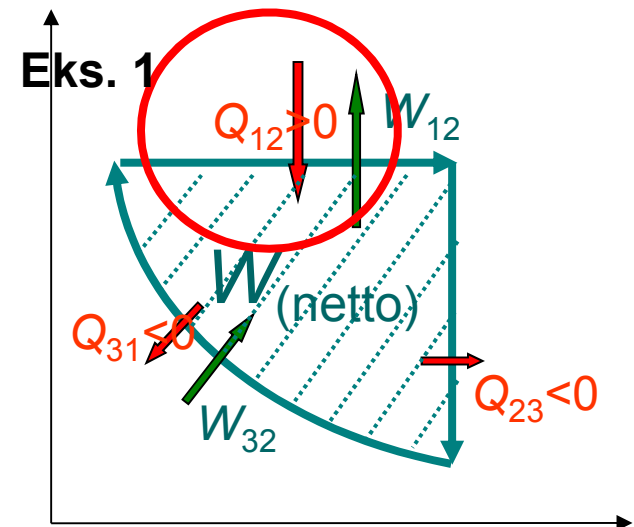


Virkningsgrad:

$$\eta = \text{nytte/kostnad}$$

$$= W/Q_{inn}$$

$$= 1 - |Q_{ut}|/Q_{inn}$$



## Eks 2. Kretsprosess med adiabat

$$\Delta U = 0$$

$$Q_{(\text{netto})} = W_{(\text{netto})}$$

$$T_2 = 2T_1$$

$$T_3 = T_1 \left(\frac{1}{2}\right)^{2/3} = T_1 \cdot 0,630$$

$$W_{12} = p_1 V_1 = nRT_1$$

$$W_{23} = 0$$

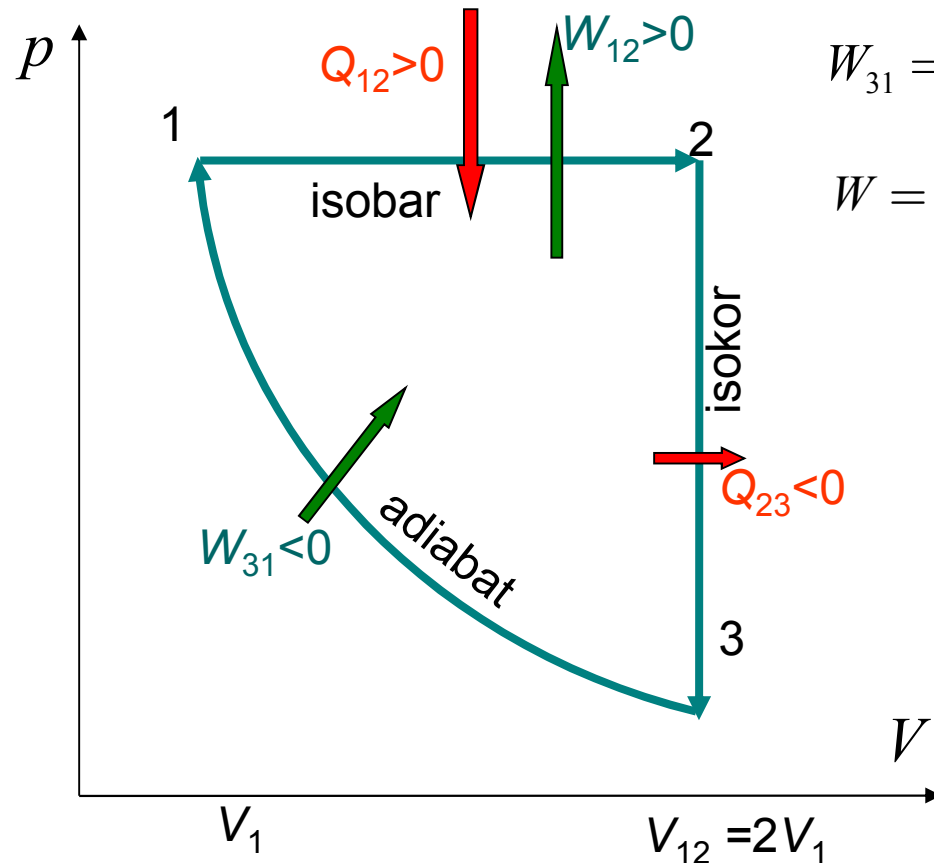
$$W_{31} = -\Delta U_{13} = -C_V n(T_1 - T_3) = -\frac{3}{2} nRT_1 \left(1 - \left(\frac{1}{2}\right)^{2/3}\right)$$

$$W = W_{12} + W_{31} = nRT_1 \frac{1}{2} \left(3 \left(\frac{1}{2}\right)^{2/3} - 1\right) = nRT_1 \cdot 0,445$$

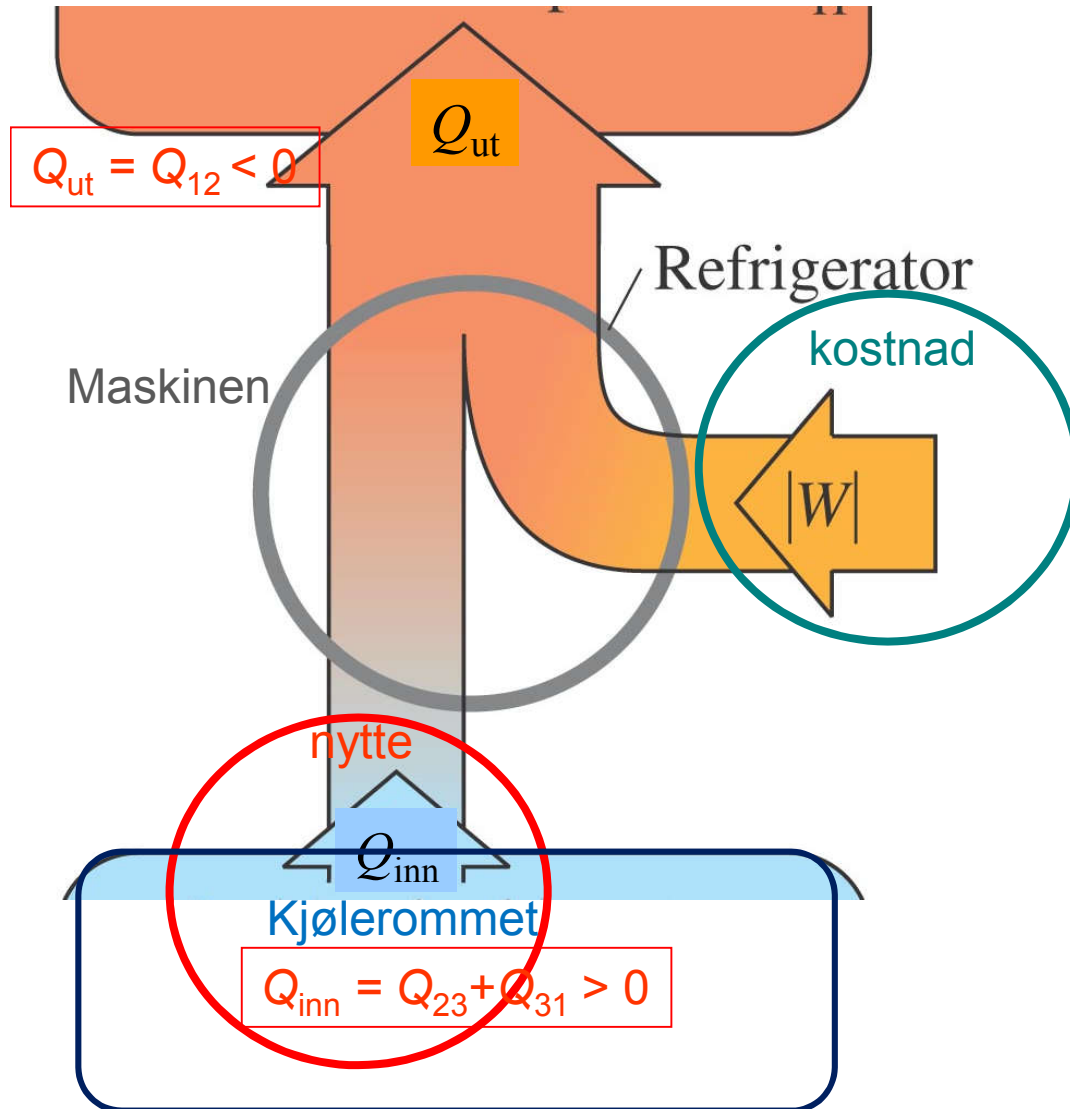
$$Q_{12} = C_p n(T_2 - T_1) = \frac{5}{2} nRT_1$$

$$Q_{23} = C_V n(T_3 - T_2) = -\frac{3}{2} nRT_1 \left(2 - \left(\frac{1}{2}\right)^{2/3}\right)$$

$$\eta = \frac{W}{Q_{12}} = \frac{nRT_1 \cdot 0,445}{nRT_1 \cdot 5/2} = 0,178$$



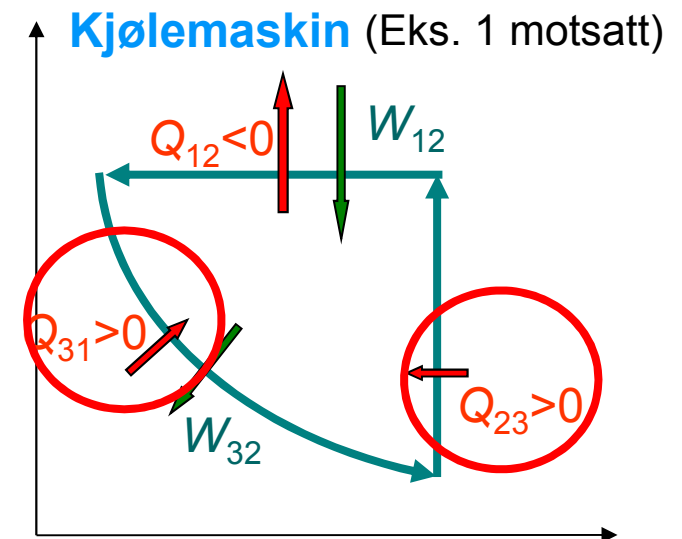
# Energiflytdiagram for kjølemaskin



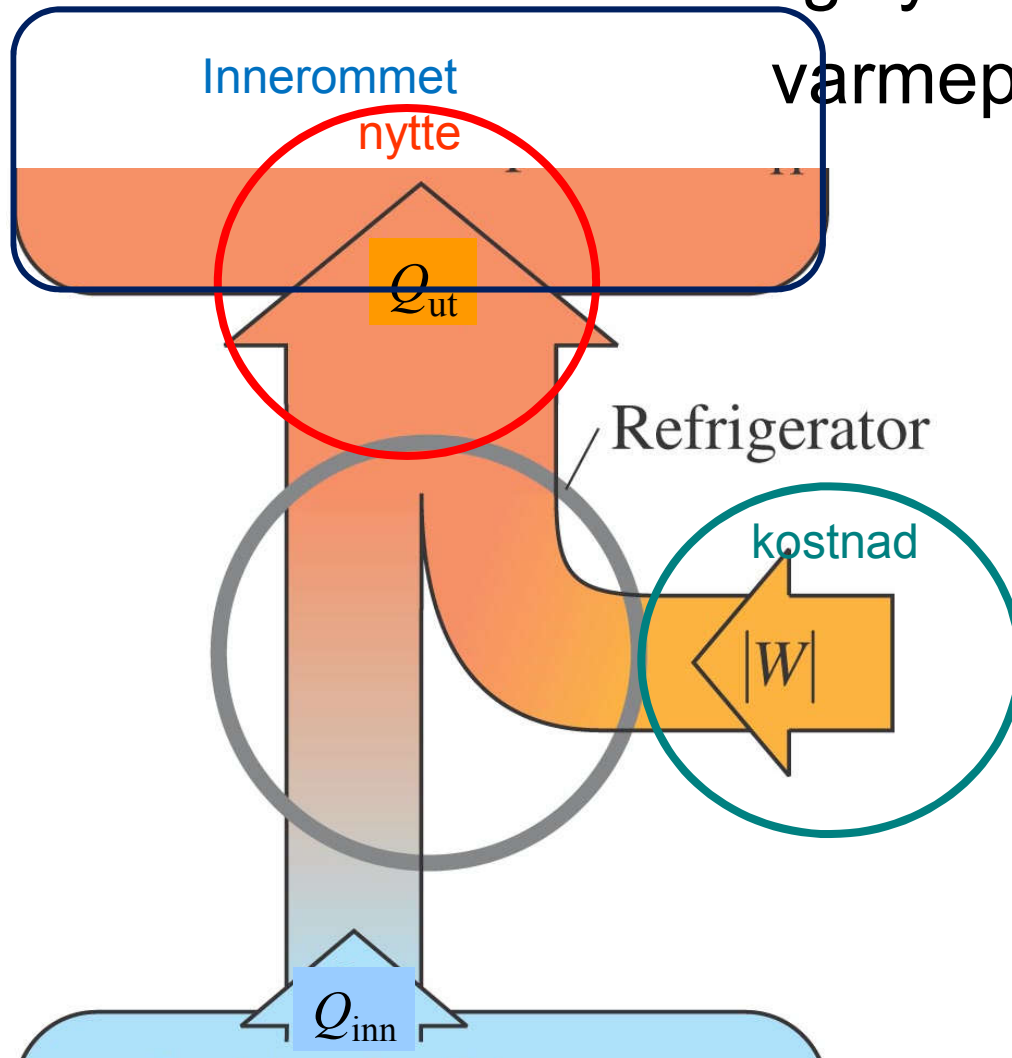
Effektfaktor:

$$\eta_K = \text{nytte/kostnad}$$

$$= |Q_{inn}| / |W|$$



# Energiflytdiagram for varmepumpe



Effektfaktor:

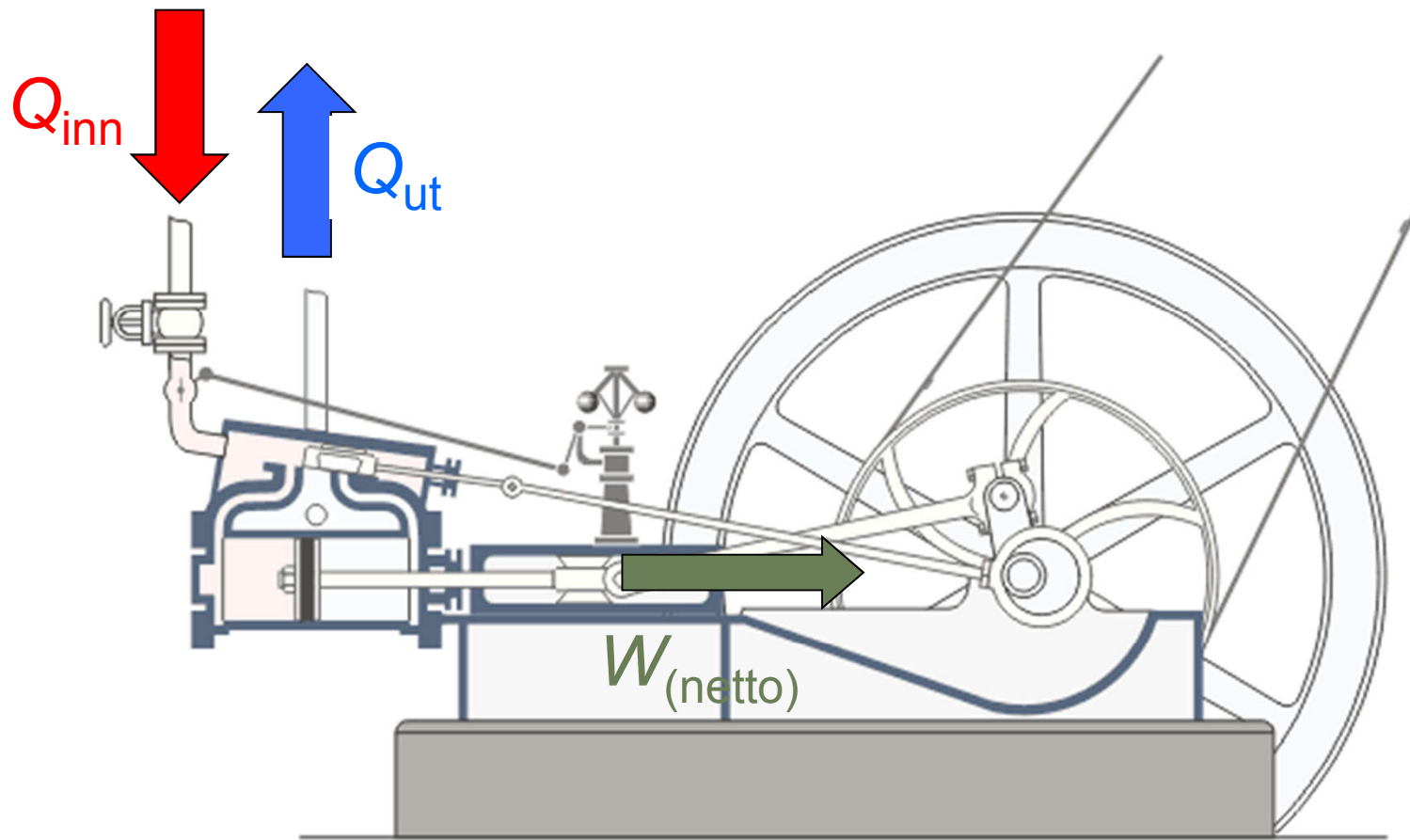
$$\eta_V = \text{nytte/kostnad}$$

$$= |Q_{ut}| / |W|$$

# Prinsipp dampmaskin

Virkningsgrad:

$$\eta = \text{nytte/kostnad} = W/Q_{\text{inn}}$$



# Varmekraftmaskiner

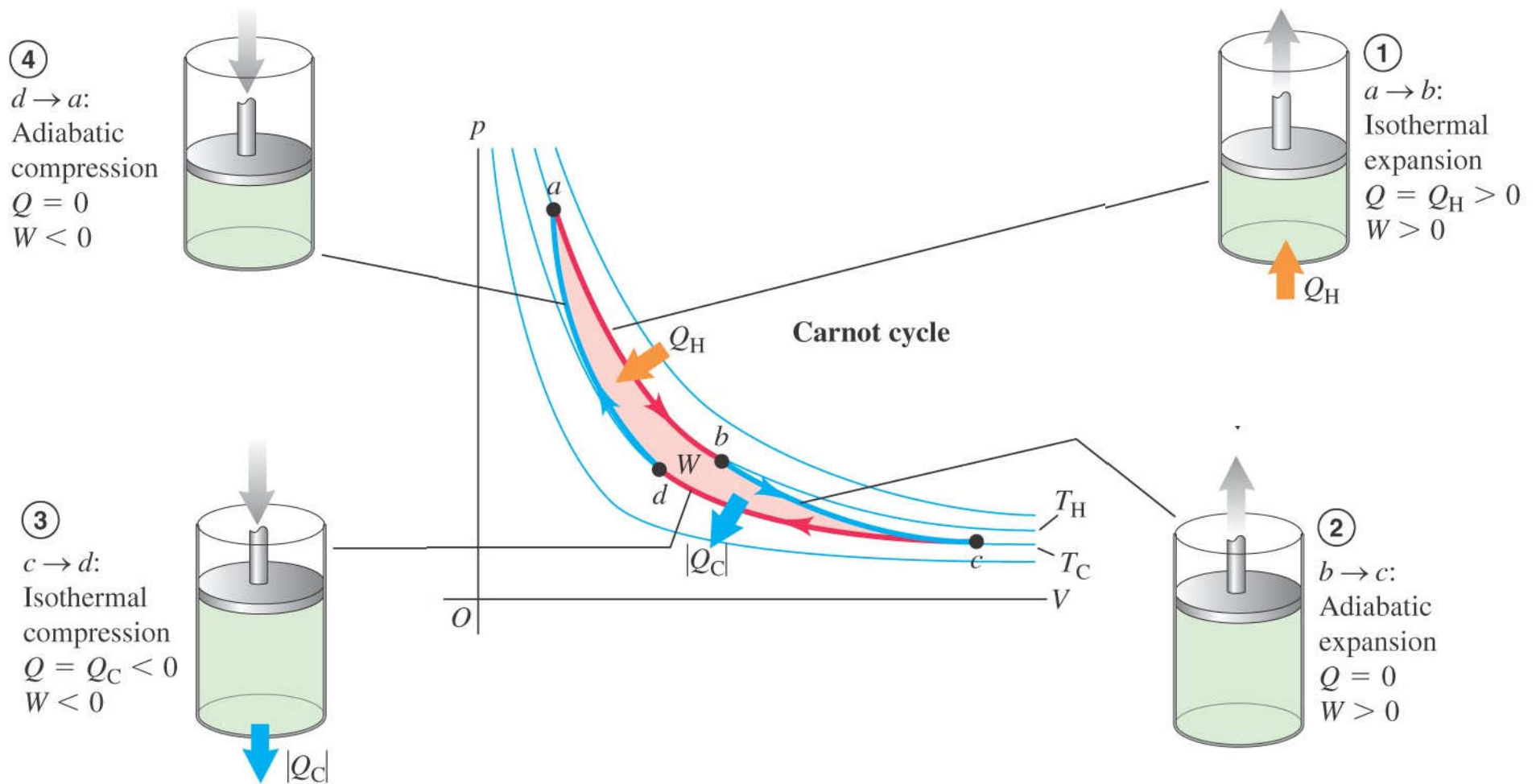
- 1698: Thomas Savery: Vannpumper i gruver
- 1712: Thomas Newcomen: Dampmaskin (ineffektiv)
- 1765: James Watt: Mer effektiv dampmaskin
- 1769: Første dampdrevne kjøretøy
- 1803: Første dampdrevne lokomotiv
- 1829: George Stephenson's "The rocket"
- 1876: Nikolaus A. Otto: 4-taktsbensinmotor  
Totaktmotor: 1881. Firetakt diesel: 1893.
- 1824: Sadi Carnot: Carnotsyklus  
(teoretisk optimale maskin)



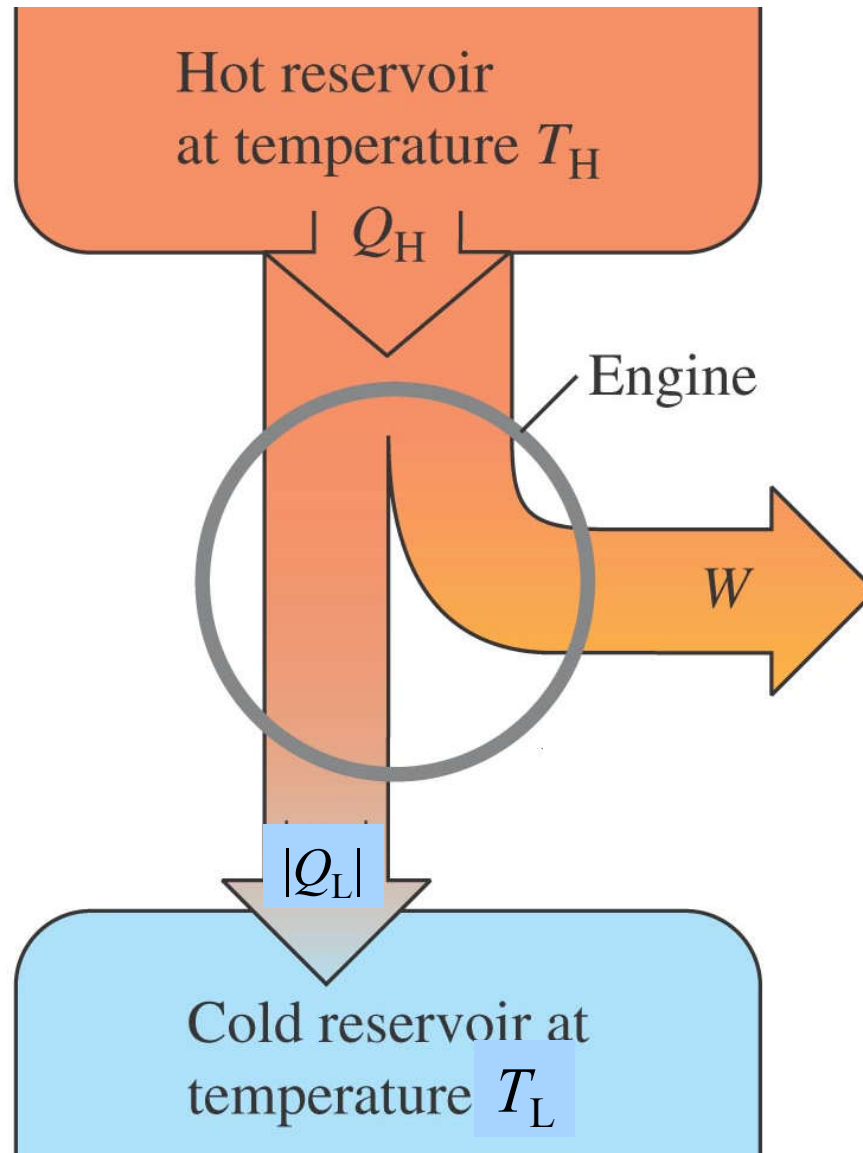
# Carnotsyklus: Reversibel varmeoverføring

ved kun to temperaturer:  $T_H$  og  $T_C$

(Sadi Carnot 1824)



# Energifyttdiagram for varmekraftmaskin (Carnot)



Virkningsgrad:

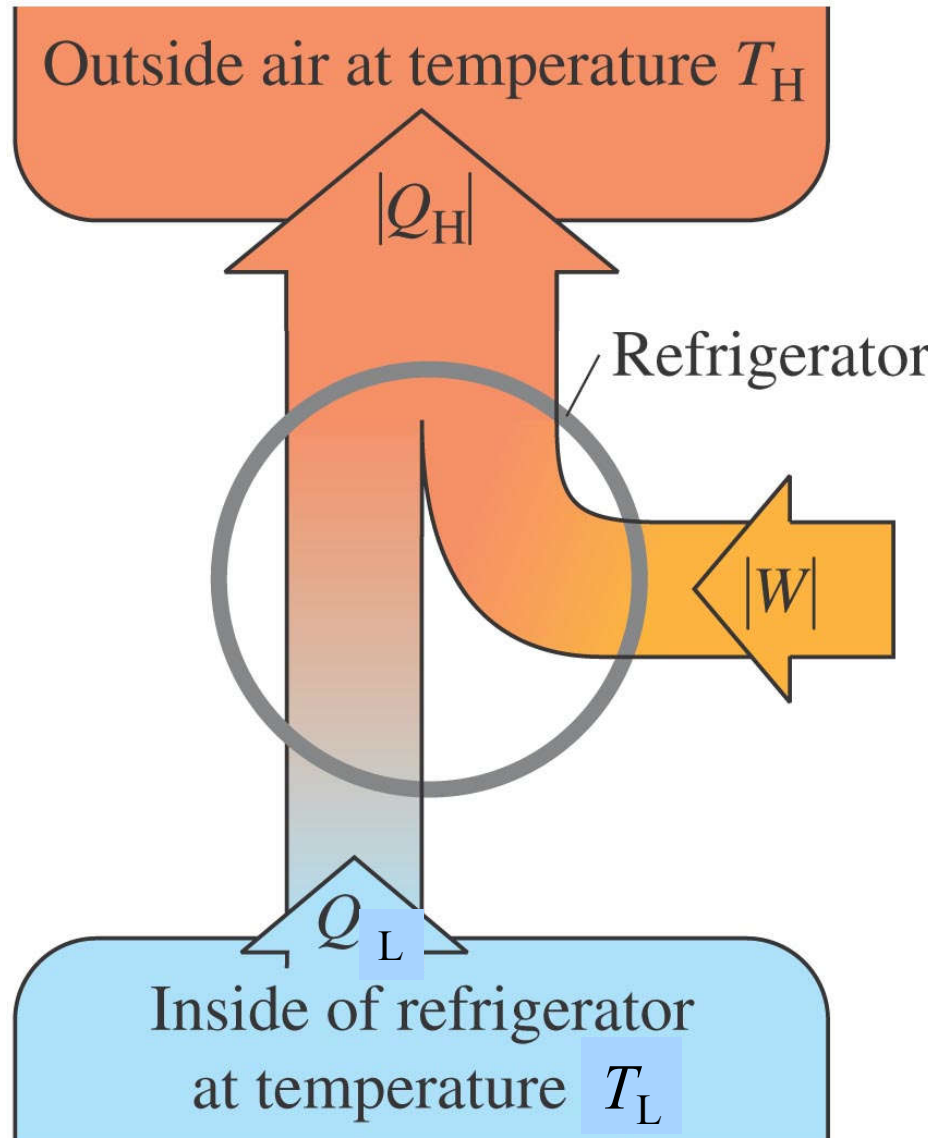
$$\eta_C = \text{nytte/kostnad}$$

$$= W/Q_H = 1 - |Q_L|/Q_H$$

Ideell gass:

$$\eta_C = 1 - T_L/T_H$$

# Energiflytdiagram for kjølemaskin (Carnot)



Effektfaktor:

$$\eta_{K,C} = \text{nytte/kostnad} \\ = |Q_L| / |W|$$

Ideell gass:

$$\eta_{K,C} = T_L / (T_H - T_L)$$

# Energiflytdiagram for varmepumpe (Carnot)

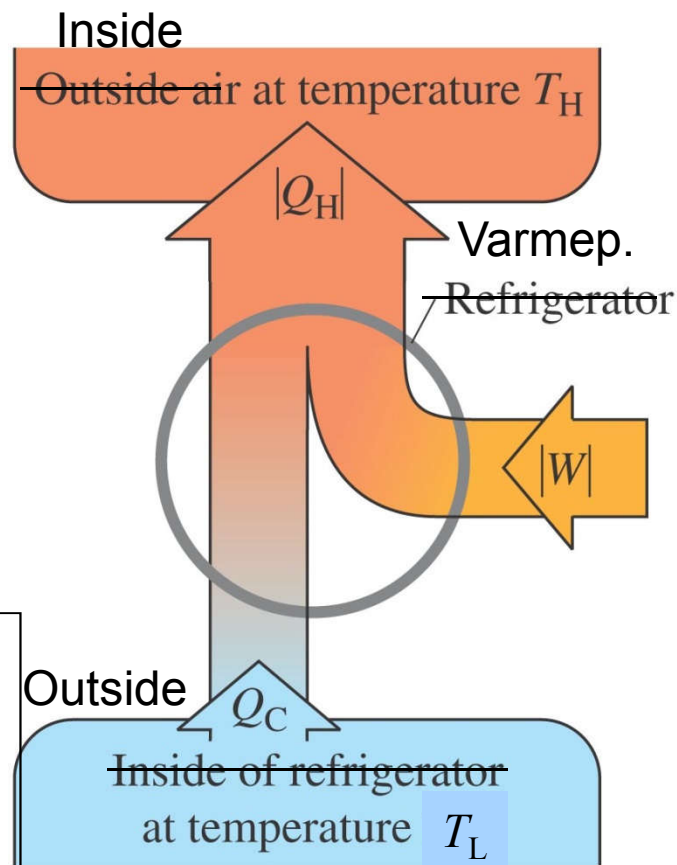
Eksempel:

$T_H$ :  
20°C  
=293K

Effektfaktor

ideell gass:

$$\eta_{V,C} = T_H / (T_H - T_L)$$



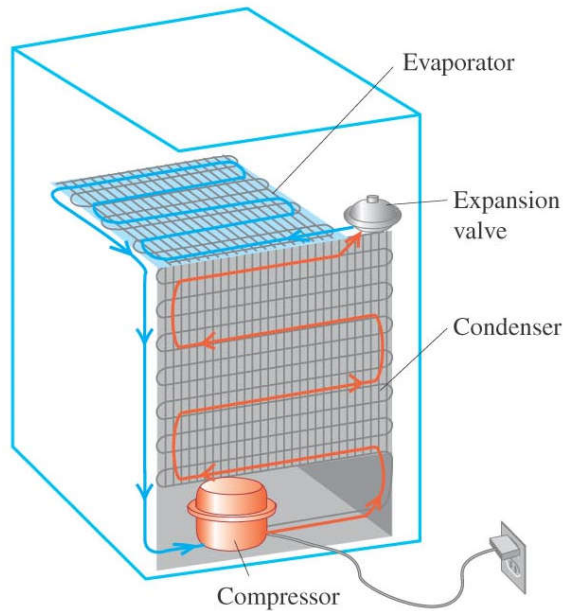
$T_L$ :

0°C =273 K	-20°C =253 K	18°C =297 K
$\eta_{V,C} =$ 293/20 =15	293/40=7,5	293/2=150 !
Reell COP= 3 – 4	2-2,5	??

Reelt er  $T_H$  (varmen inne i varmeveksleren) mye høyere enn innetemp, f. eks. 35-40°C.

Dette gir lavere  $\eta_{V,C}$

# Kjøleskap = kjølemaskin

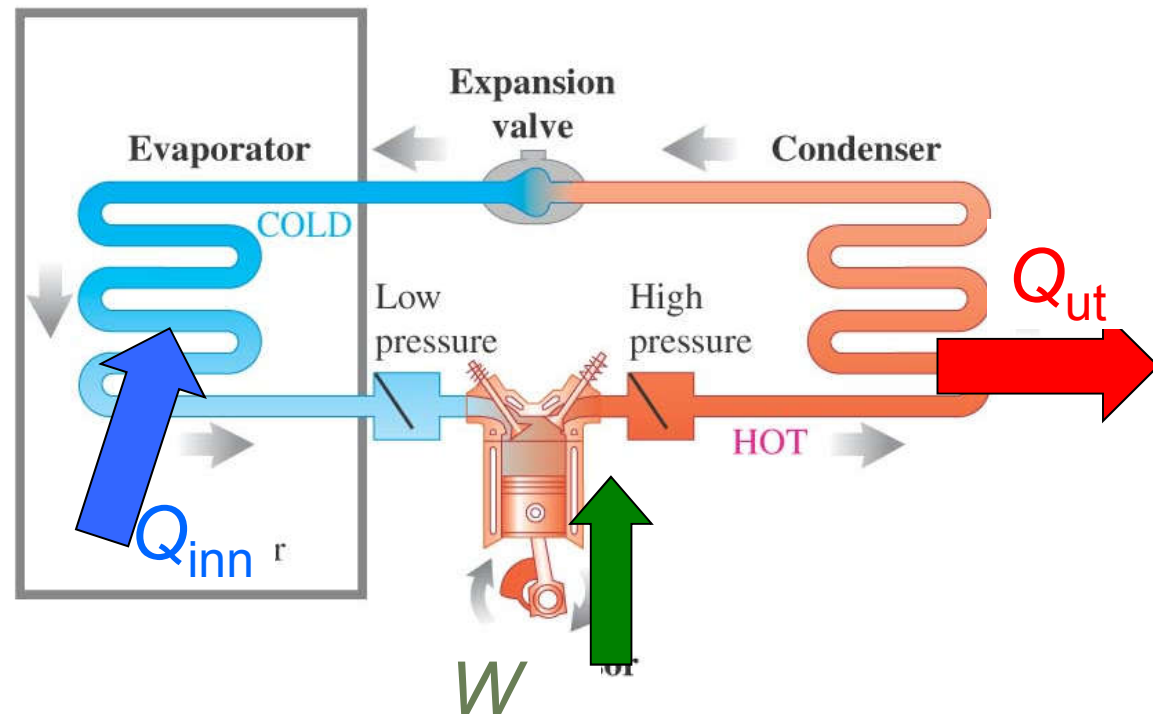


Effektfaktor:

$$\eta = \text{nytte/kostnad}$$

$$= |Q_{\text{inn}}| / |W|$$

Prinsipp:



# Kretsprosesser, 2. hovedsetning. Så langt:

## Reversible prosesser:

Termisk likevekt under hele prosessen: kurver på likevektsflater.

Langsomt og kontrollert. Tilnærmet umulig i praksis, men likevel svært viktig.

**Kretsprosess:** Start = Slutt  $\Delta U = 0$   $Q_{(\text{netto})} = W_{(\text{netto})}$

Virkningsgrad  $\eta = \text{nytte/kostnad} = W/Q_{\text{inn}}$

Kjølefaktor (effektfaktor):  $\eta_K = \text{nytte/kostnad} = |Q_{\text{inn}}| / |W|$

**Isokor:**  $V = \text{konst.}$   $W = 0$ ;  $Q = \Delta U = C_V \Delta T$

**Isobar:**  $p = \text{konst.}$   $W = p(V_2 - V_1)$ ;  $Q = C_p (T_2 - T_1)$

**Isoterm:**  $T = \text{konst.}$   $W = nRT \ln(V_2/V_1)$  Id.gass:  $\Delta U = 0$ ;  $Q = W$

**Adiabat:** Ingen varmeutveksling med omgivelser:  $Q = 0 \Rightarrow \Delta U = -W$

Dvs. alt arbeid gjøres på bekostning av indre energi.

$W = -\Delta U = -C_V n (T_2 - T_1) = -1/(\gamma - 1) (p_2 V_2 - p_1 V_1)$

Prosesslikninger id. gass:  $pV^\gamma = \text{konst.}$   $TV^{\gamma-1} = \text{konst.}$   $T^\gamma p^{1-\gamma} = \text{konst.}$

## Carnotprosessen:

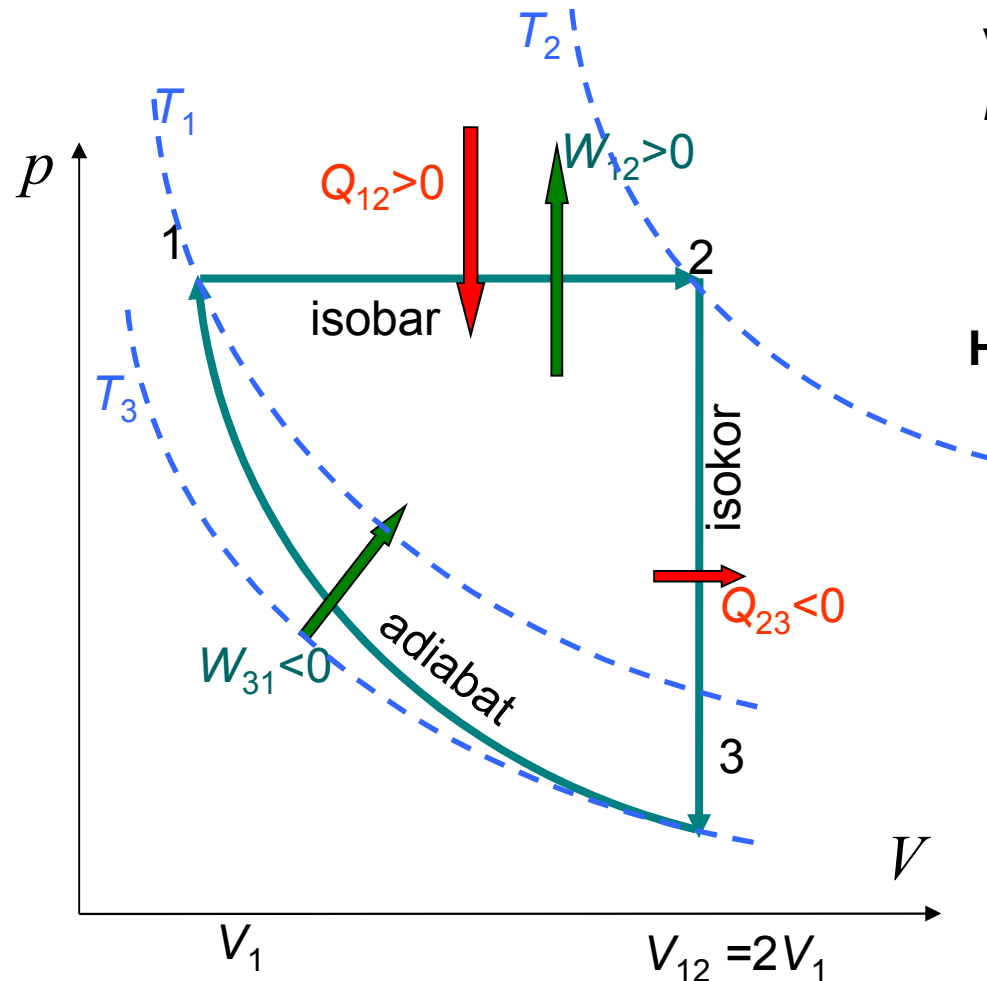
Mest effektive prosess mellom to temperaturer  $T_H$  og  $T_L$ ,

To isotermer og to adiabater.

$$\eta_C = \eta_{\text{max}} = 1 - Q_L/Q_H = 1 - T_L/T_H \quad \text{Ideell gass}$$

$$\eta_{K,C} = \eta_{\text{max}} = Q_L/(Q_H - Q_L) = T_L/(T_H - T_L)$$

## Eks. 2. Kretsprosess med adiabat



$$T_2 = 2T_1$$

$$T_3 = T_1 \left( \frac{1}{2} \right)^{2/3} = T_1 \cdot 0,630$$

Vi fant:  
 $\eta = 0,18$

$$T_2 > T_1 > T_3$$

**Hvis vi heller lager en carnotprosess:**

Carnot mellom  $T_2$  og  $T_3$ :

$$\eta_C = 1 - T_3/T_2 = 0,68$$

eller Carnot mellom  $T_1$  og  $T_3$ :

$$\eta_C = 1 - T_3/T_1 = 0,37$$

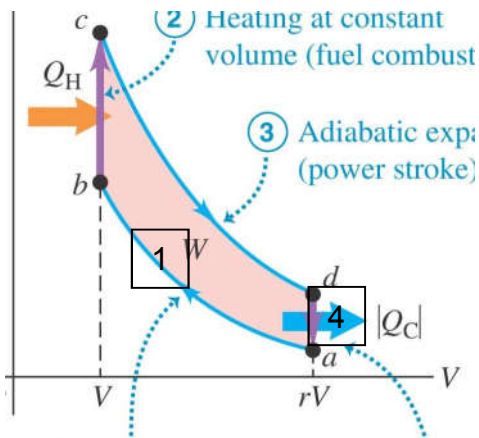
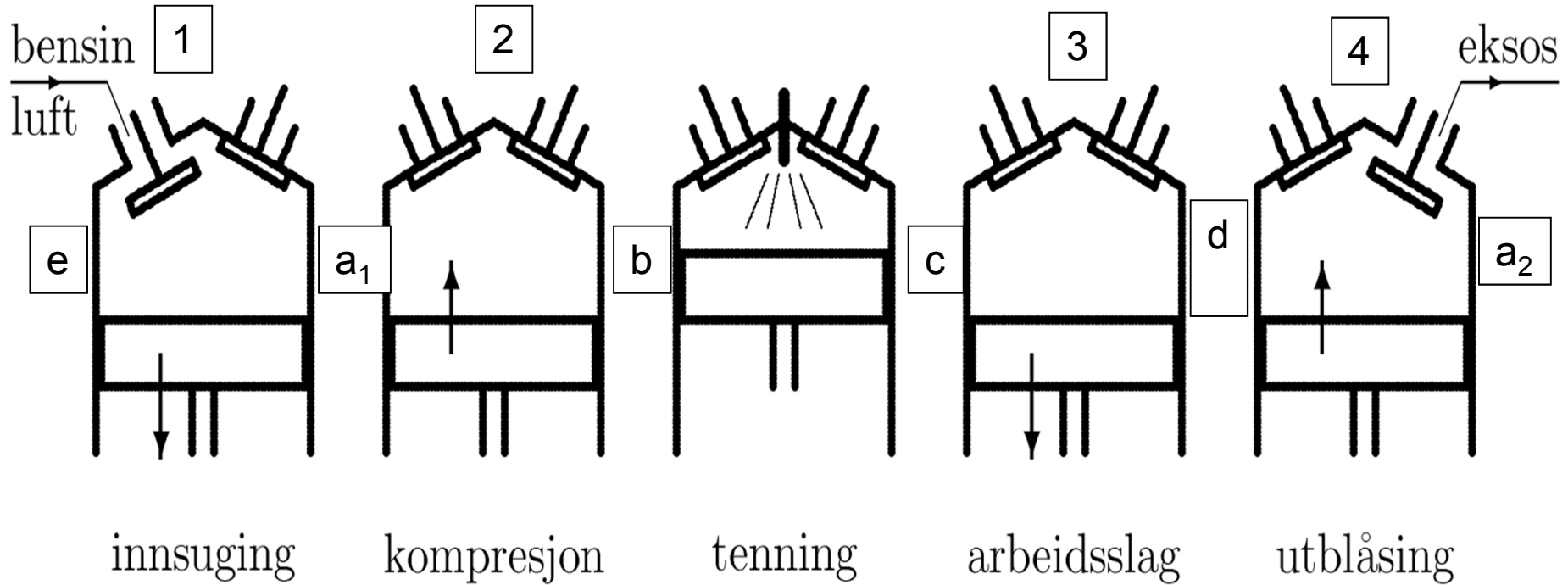
eller Carnot mellom  $T_2$  og  $T_1$ :

$$\eta_C = 1 - T_1/T_2 = 0,50$$

Alle bedre enn 0,18

# Otto-syklus.

Nikolaus A. Otto bygde i 1876  
den første fungerende 4-taktsmotor (bensinmotor)



$$\eta_{\text{Otto}} = 1 - 1/r^{\gamma-1}$$

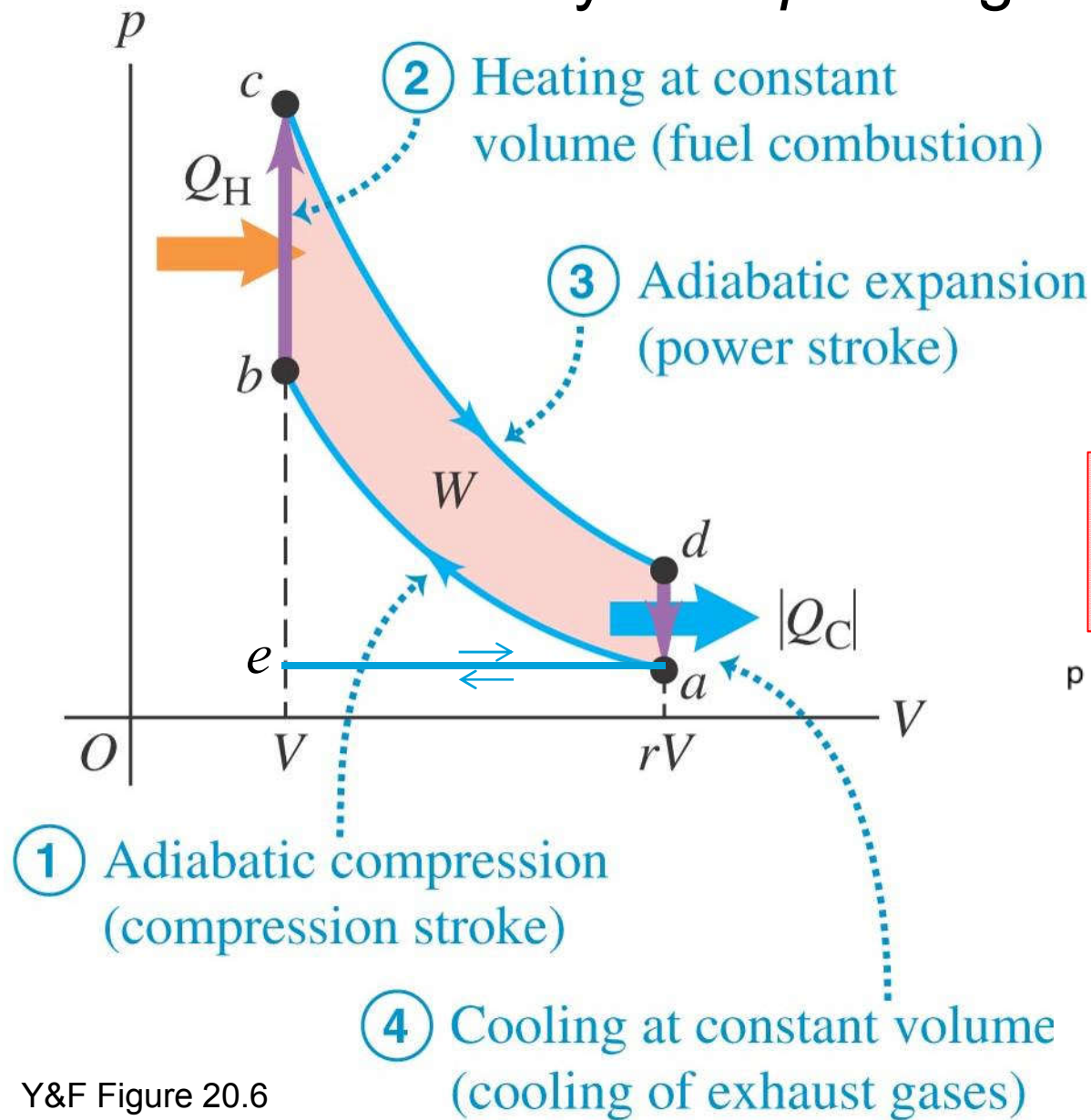
der

$$r = V_2/V_1 =$$

kompresjonsforhold



# Otto-syklus i $pV$ -diagram.



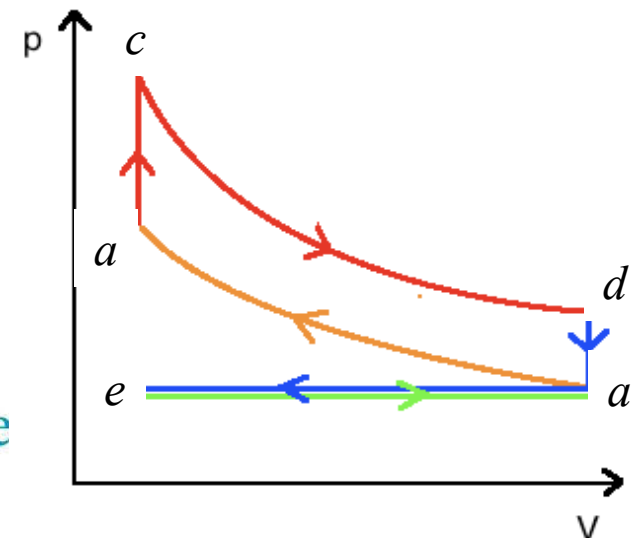
$$\eta_{\text{Otto}} = 1 - 1/r^{\gamma-1}$$

der

$$r = V_2/V_1$$

= kompresjonsforhold

Bevis i Y&F - likn. (20.6) eller Eksempel «Otto-syklus» på nettsider.



Y&F Figure 20.6

## Virkningsgrad for ulike varmekraftverk (energiverk):

	kullfyrt	gassfyrt	vannkraft
$T_H \approx$	640 K	900 K	
$T_L$ (kjølevann) $\approx$	300 K	300 K	
$\eta_C = 1 - T_L/T_H \approx$	0,5	0,7	
$\eta_{\text{reell}}$	0,4	0,6	0,95

## Sammenlikning mekanisk (høyde)energi og varme:

1000 m vannfall for 1 liter vann (1 kg) gir utløst høydeenergi:

$$\begin{aligned} E_p &= mgh \\ &= 1 \text{ kg} \cdot 9,81 \text{ m/s}^2 \cdot 1000 \text{ m} \\ &= 9,81 \text{ kJ} \end{aligned}$$



Hvis denne energien brukes til å varme opp vannet:

$$E_p = Q = C' m \Delta T \quad \text{Varmekap} = C' = 4,2 \text{ kJ}/(\text{kg K})$$

$$\Rightarrow \text{Temp.økning} = \Delta T = 9,81/4,2 \text{ K} = 2,3 \text{ K}$$

Sett fra motsatt side:

**2,3 °C avkjøling** gir ut samme energi som fall 1000 m

# Høyverdig energi

( $\approx 100\%$  utnyttelse til mekanisk energi):

- Oppspent fjær
- Pot.en. i vannmagasin
- Elektrisk energi i batteri og lignende

# Lavverdig energi

(0-60% utnyttelse til mekanisk energi):

- Varme, f.eks. i vannet i vannmagasin eller i sjøvann  
Store mengder, men vanskeligere å overføre til mekanisk energi.
  - Mulighetene beskrevet i **2. hovedsetning**
  - Gjøres i **varmekraftmaskin**
  - Mulighetene måles med **entropi**

# Kretsprosesser. 2. hovedsetning

Reversible og irreversible prosesser (20.1)

Adiabatisk prosess (19.8)

Kretsprosesser:

varmekraftmaskiner (20.2+3)

kjølemaskiner (20.4)

Carnotsyklusen (20.6)

Eks: Ottosyklus (20.3)

2. hovedsetning (20.5)

Carnots teorem og Carnots (u)likhet

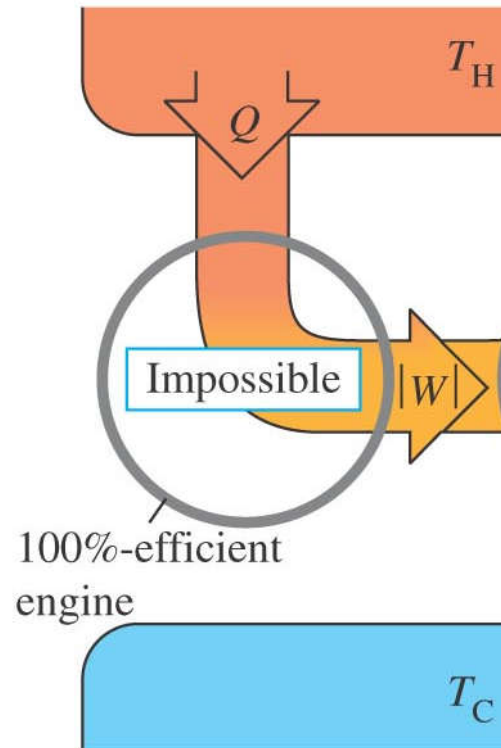
I dag

Entropi (20.7)

Entropien mikroskopisk forklart (20.8)

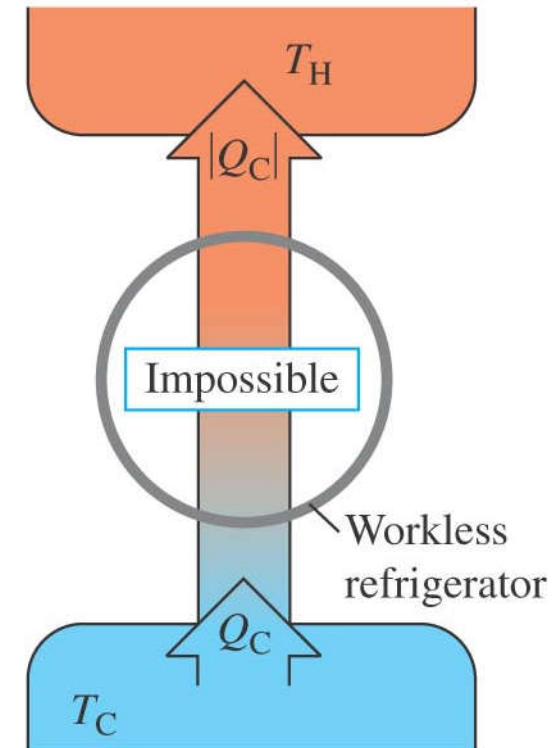
## 2. hovedsetning

Kelvins formulering

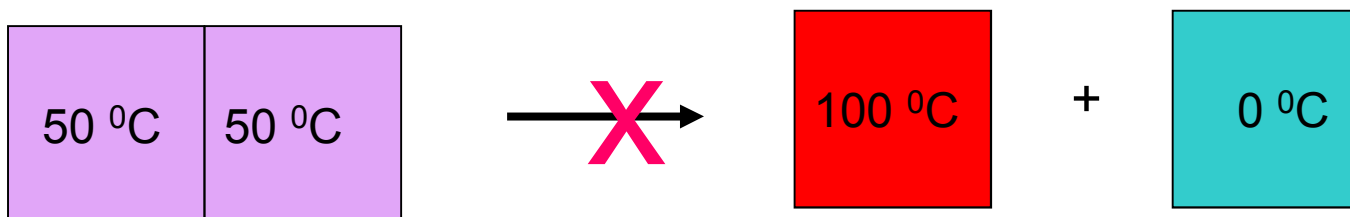
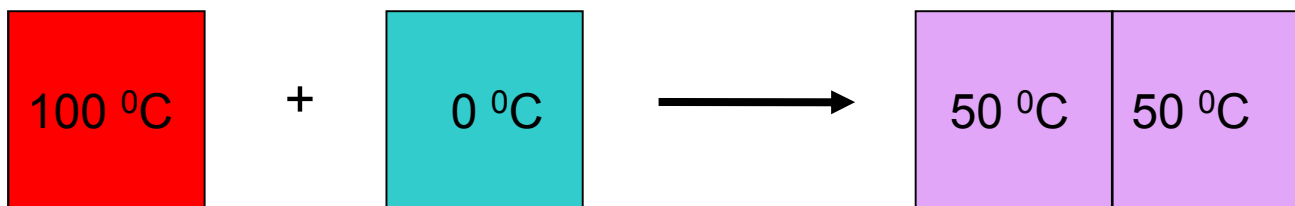


is equivalent to

Clausius formulering



Rudolf Clausius (1822-88) tysk fysiker  
Lord Kelvin (1824-1907) irsk matem/fysiker (=William Thompson)  
Sadi Carnot (1796-1832) fransk fysiker



**Ingen har observert varme strømme fra kaldt til varmt legeme**

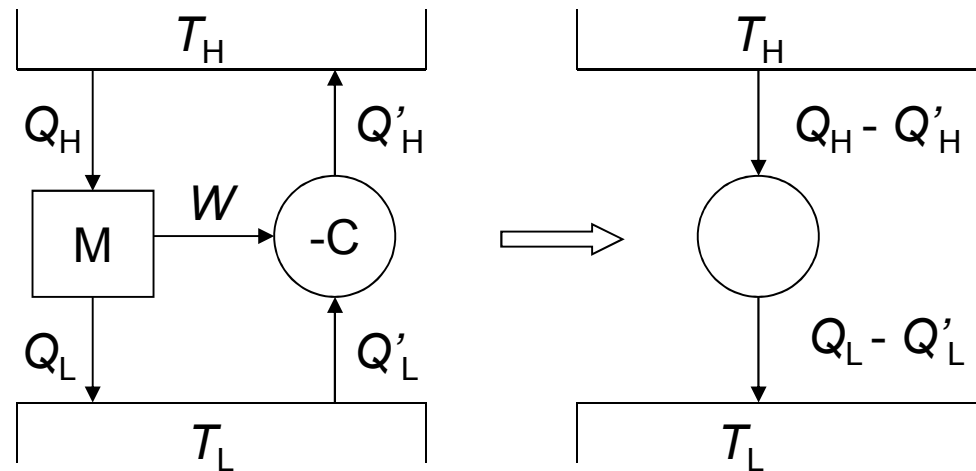
**<=>**

**Clausius formulering av  
termodynamikkens 2. hovedsetning**

# Carnots to teorem

1. For en carnotprosess er  $\eta = \eta_C = 1 - T_L/T_H$  uansett arbeidssubstans.
2. Ingen kretsprosess mellom to reservoar kan ha større  $\eta$  enn  $\eta_C = 1 - T_L/T_H$

Bevis for 2:

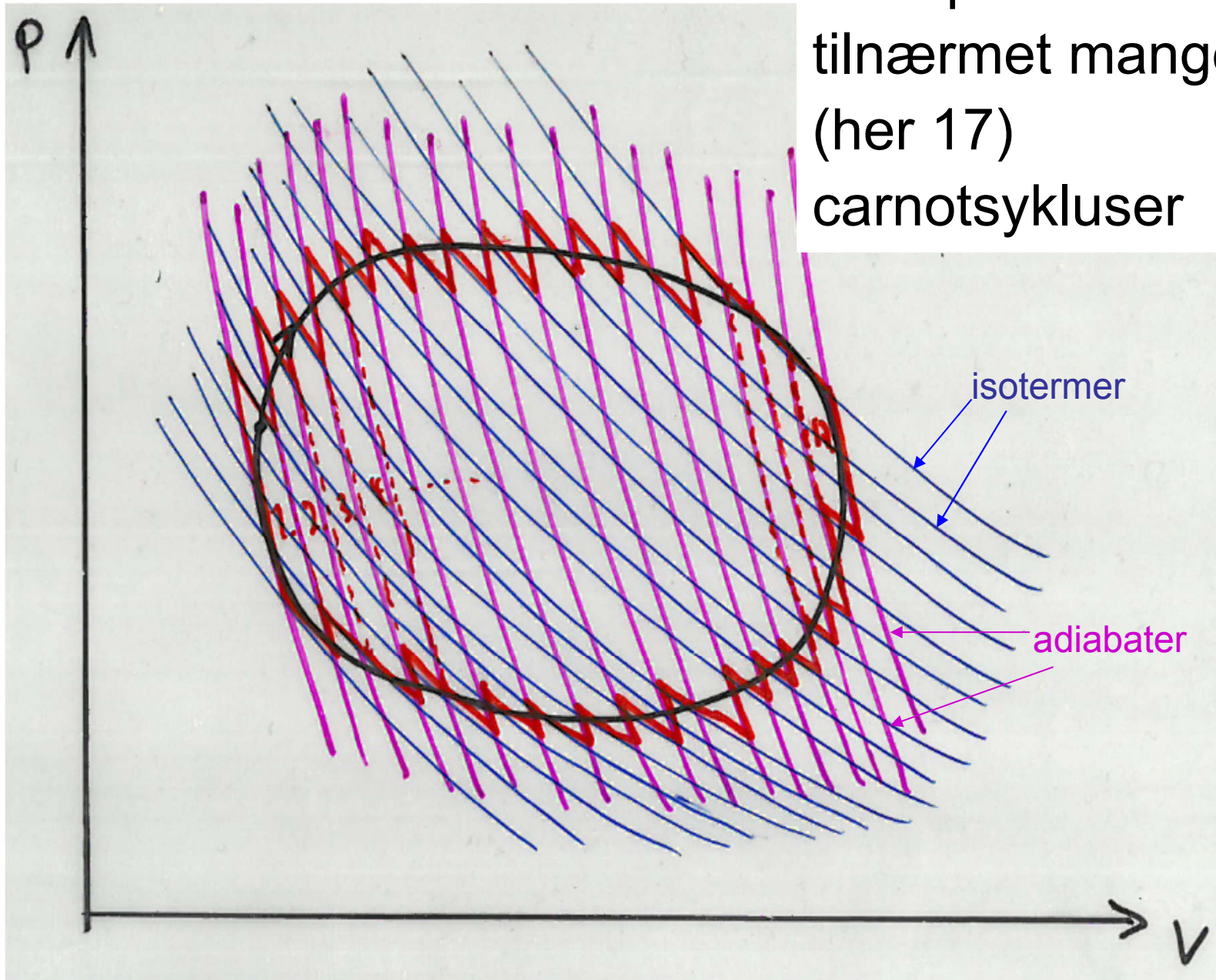


$$(2.H-C) \Rightarrow Q_H \geq Q'_H$$

$$\Rightarrow \eta_M = W/Q_H \leq W/Q'_H = \eta_C$$

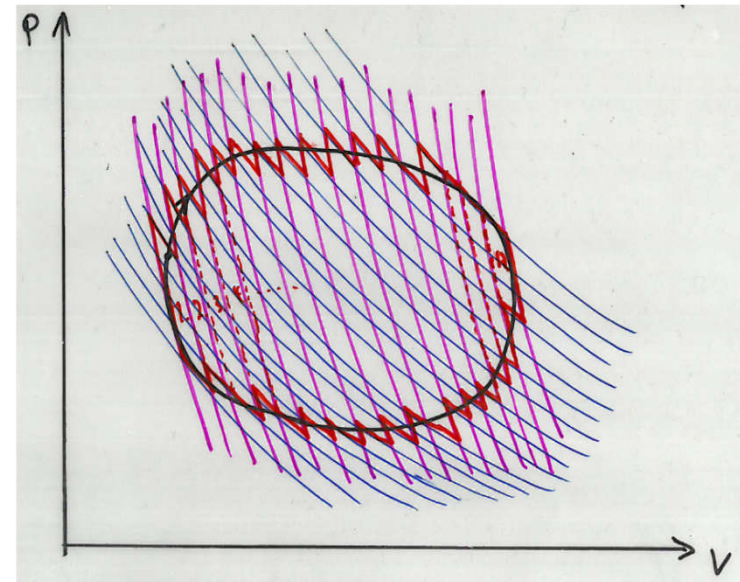


Kretsprocess  
tilnærmet mange  
(her 17)  
carnotsykluser



# Clausius (u)likhet for kretsprosesser.

- Carnotprosesser ( $T_H$  og  $T_L$ ):  $Q_H/T_H + Q_L/T_L = 0$
- Mange carnotprosesser:  $\sum Q_k/T_k = 0$
- Mange (irreversible) prosesser :  $\sum Q_k/T_k < 0$
- $\infty$  mange infinitesimale prosesser:  
 $\int dQ/T = 0$  reversibel kretsprosess  
 $\int dQ/T < 0$  irreversibel kretsprosess



# Clausius ulikhet og entropi.

$$\int \dot{d}Q/T = 0 \quad \text{reversibel kretsprosess}$$

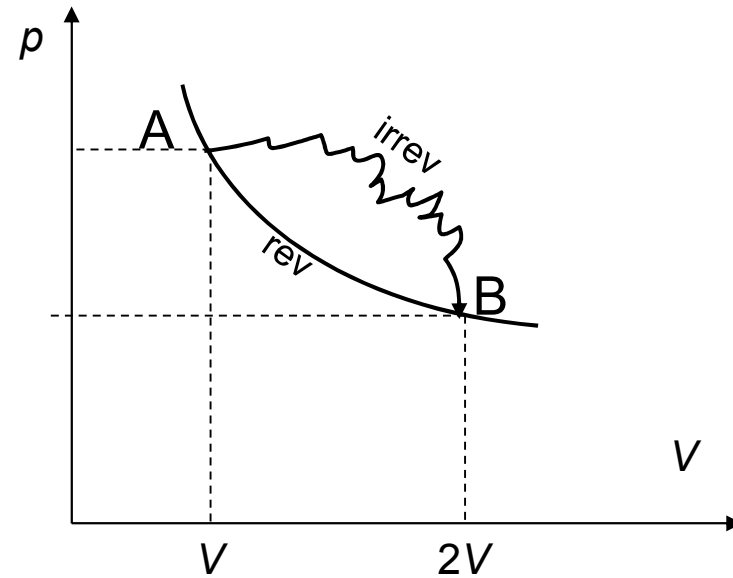
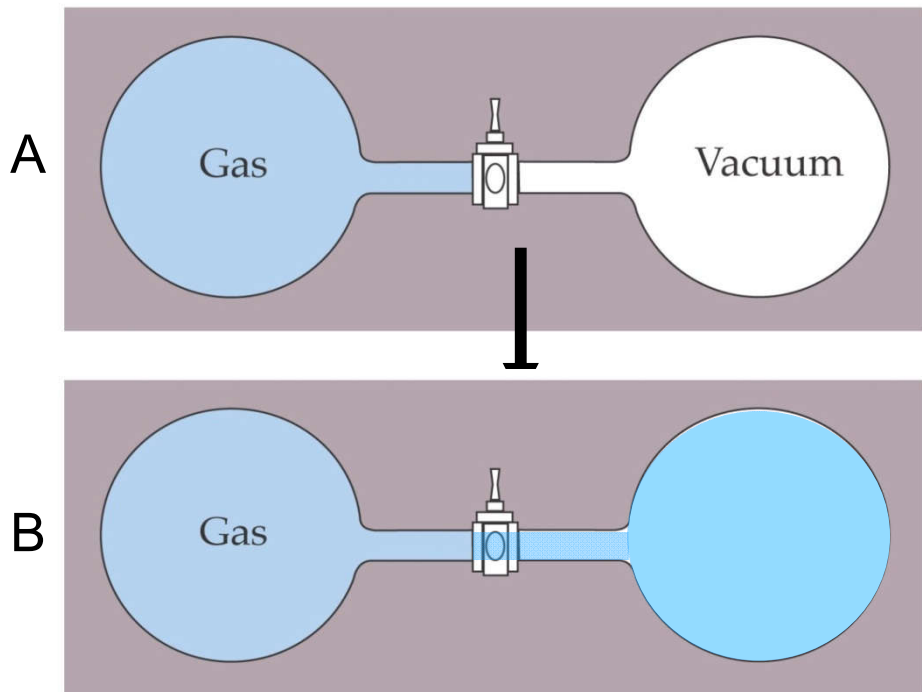
$$\int \dot{d}Q/T < 0 \quad \text{irreversibel kretsprosess}$$

Def. entropi:

$$dS = \dot{d}Q_{\text{rev}}/T \quad \text{eller} \quad \Delta S = \int \dot{d}Q_{\text{rev}}/T$$

$S$  er tilstandsfunksjon, ikke avhengig vegen.

Beregning må gjøres via rev. prosess, men resultatet er det samme uansett, når start- og slutttilstand er gitt.

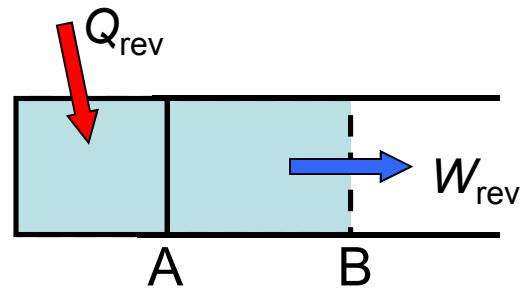
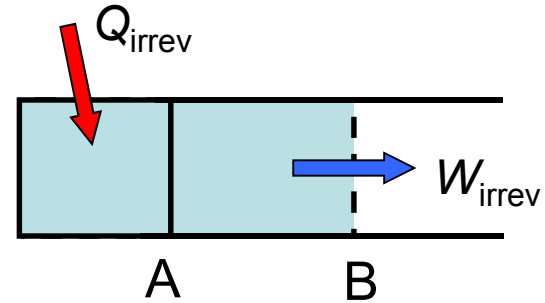
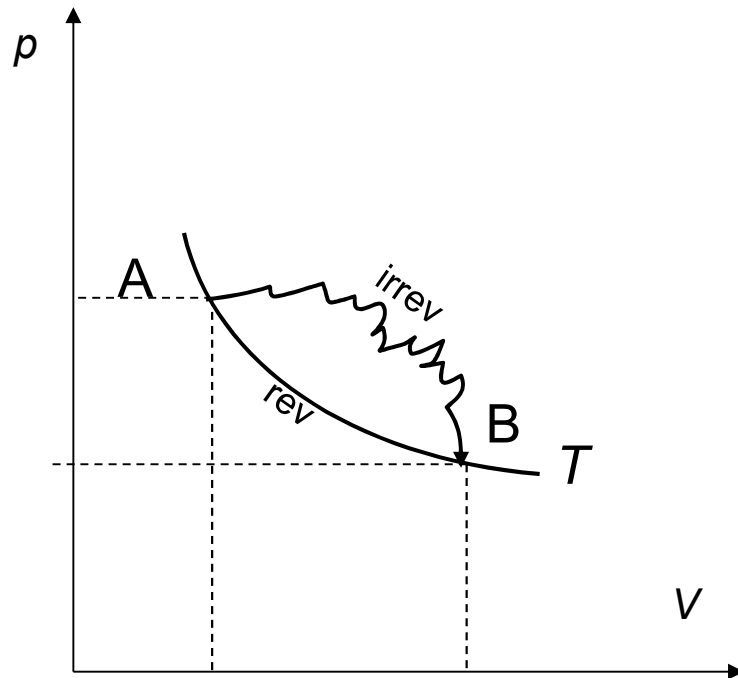


$$\int_A^B \frac{dQ_{\text{irr}}}{T} < \Delta S_{AB}$$

**1) Fri, adiabatisk ekspansjon:**  $0 < \Delta S_{AB}$

Entropien øker

## 2) Irreversibel isoterm prosess:



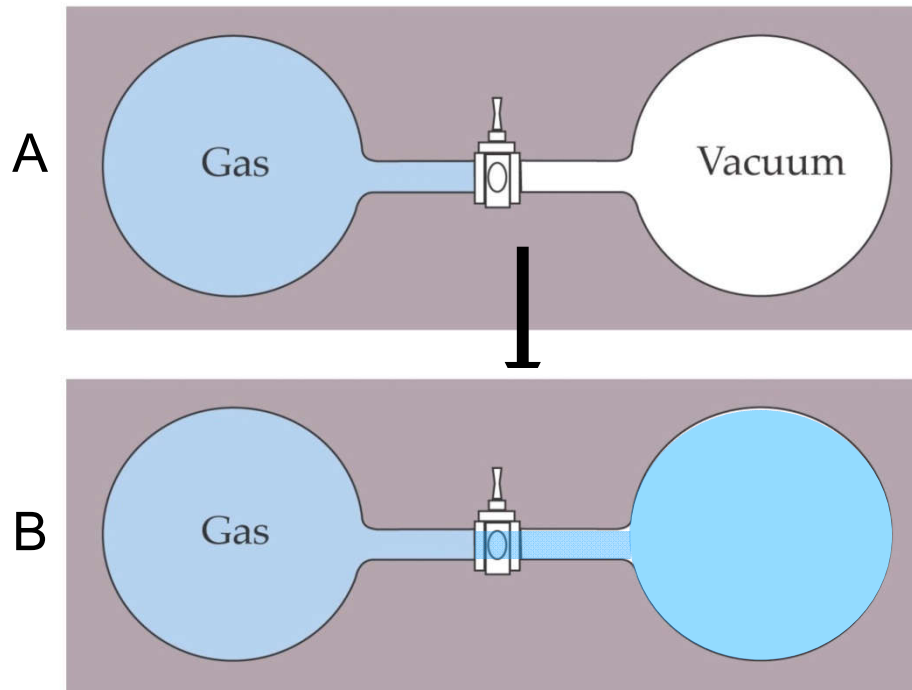
$$Q_{\text{irrev}} < Q_{\text{rev}} = T \Delta S_{AB}$$

$$W_{\text{irrev}} < W_{\text{rev}}$$

men

$$\Delta U = Q_{\text{rev}} - W_{\text{rev}} = Q_{\text{irrev}} - W_{\text{irrev}} = 0$$

# Fri, adiabatisk ekspansjon:



Ikke termisk likevekt under prosessen.

$\Delta S_{AB}$  må beregnes fra **reversibel prosess** med samme start- og slutttilstand.

-- Hva slags reversibel prosess?

Isolert  $\Rightarrow$  adiabatisk  $\Rightarrow Q_{\text{irr}} = 0$

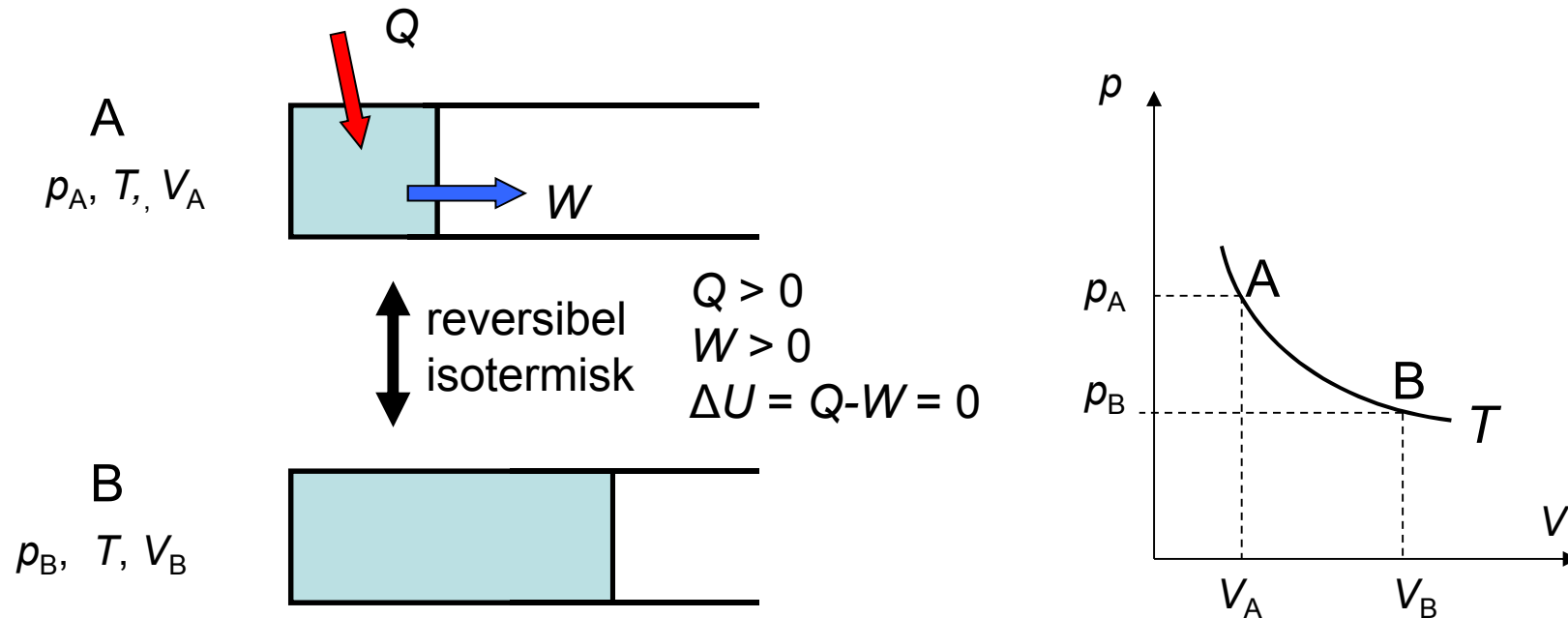
Vakuu  $\Rightarrow W = p\Delta V = 0 \quad \Delta V = 0$

(1.H)  $\Rightarrow \Delta U = Q - W = 0$

$\Rightarrow$  uendra temperatur (ideell gass)

Dvs. må erstattes av en **isoterm**

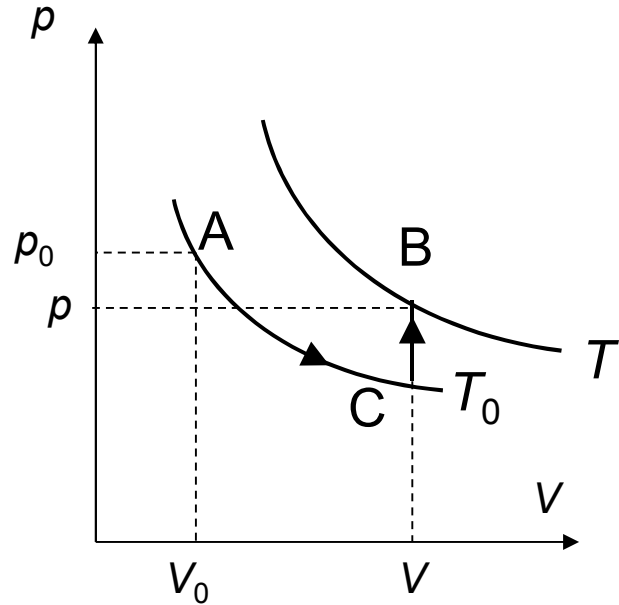
# Eks.1. $\Delta S_{AB}$ i reversibel isoterm prosess:



Idealgass:  $\Delta S_{AB} = nR \ln V_B/V_A$

# Eks. 1+2

## => Entropifunksjon ideell gass



Generell prosess  $A(p_0, V_0, T_0) \rightarrow B(p, V, T)$

= isoterm A-C + isokor C-B

$$\Delta S_{AC} = nR \ln V_C/V_A \quad \Delta S_{CB} = nC_V \ln T_B/T_C$$

Gir oss  $S(T, V)$  for ideell gass:

$$S(T, V) = S_0(T_0, V_0) + nR \ln V/V_0 + nC_V \ln T/T_0 \quad (1A)$$

$nRT = pV$  og  $C_p - C_V = R$  gir oss videre

$$S(p, V) = S_0(p_0, V_0) + nC_p \ln V/V_0 + nC_V \ln p/p_0 \quad (1B)$$

$$S(T, p) = S_0(T_0, p_0) + nC_p \ln T/T_0 - nR \ln p/p_0 \quad (1C)$$



# Tilstandsfunksjoner

Indre energi	$U(T, V)$	Ideell gass	$= C_V n T$	vdWaal: $U(T, V) = C_V n T - \frac{an^2}{V}$
Trykk	$p(T, V)$		$= nRT/V$	
Temperatur	$T(p, V)$		$= pV/nR$	
Entropi	$S(T, V)$		$= S_0(T_0, V_0) + nR \ln V/V_0 + nC_V \ln T/T_0$	
	- to frie variable			
	f.eks. $S(T, V), S(p, V)$	eller	$S(T, p)$	
	f.eks. $T(p, V), T(p, S)$	eller	$T(V, S)$	osv.

Andre (ikke pensum):

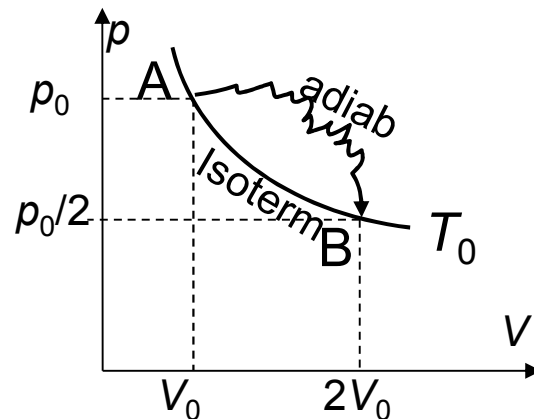
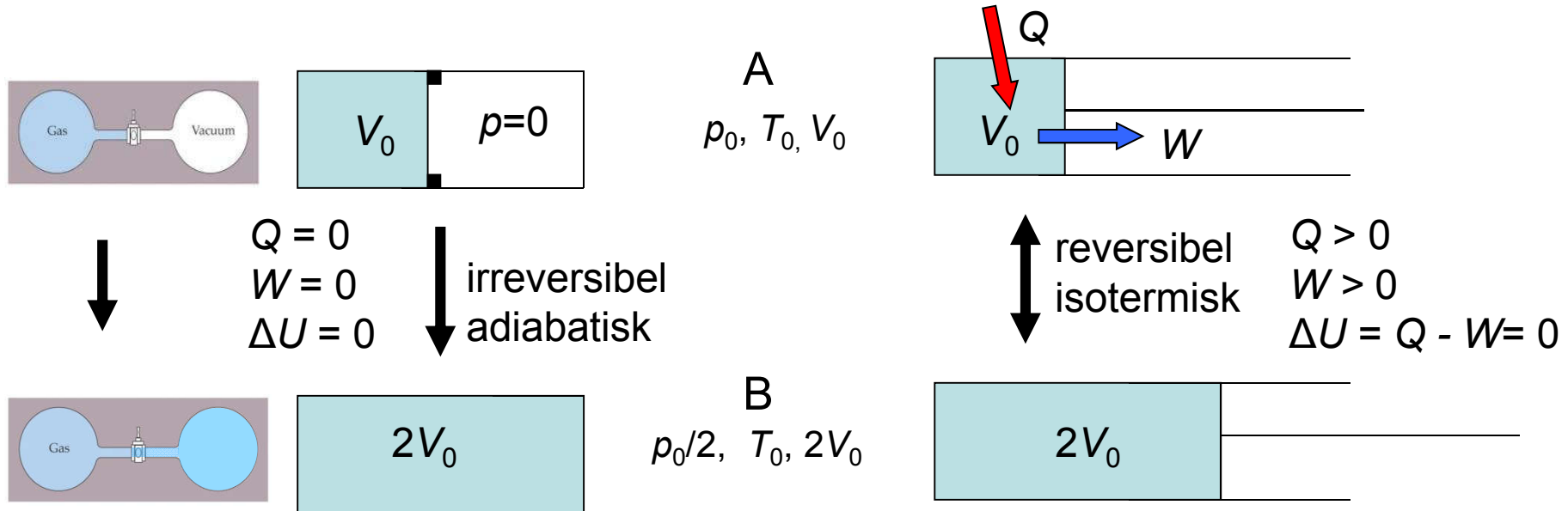
Entalpi  $H = U + pV$

Helmholtz fri energi  $F = U - TS$

Gibbs fri energi  $G = H - TS$

# Eks. 3. Irreversibel ekspansjon

Ikke termisk likevekt under prosessen, entropien må beregnes fra annen prosess med samme start- og slutttilstand.



Fra (1A) eller Eks. 1:

$$\Delta S_{AB} = nR \ln 2$$

Irrev:  $Q=0, W=0$

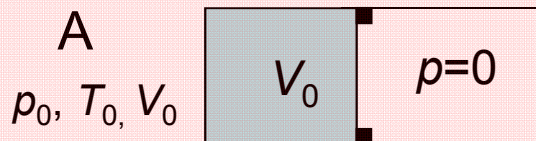
$\Delta S_{\text{tot}} > 0 \Rightarrow$  kan ikke komme tilbake

Rev:  $Q=T\Delta S > 0, W = Q > 0$

$\Delta S_{\text{tot}} = 0 \Rightarrow$  kan komme tilbake

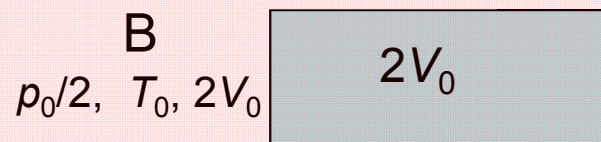
### Eks. 3. Irreversibel adiabatisk utvidelse

Nettopp beregnet:

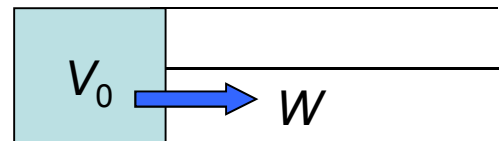


$Q = 0$   
 $W = 0$   
 $\Delta U = 0$   
 $\Delta S = nR \ln 2$

irreversibel adiabatisk  
Temp. konst.

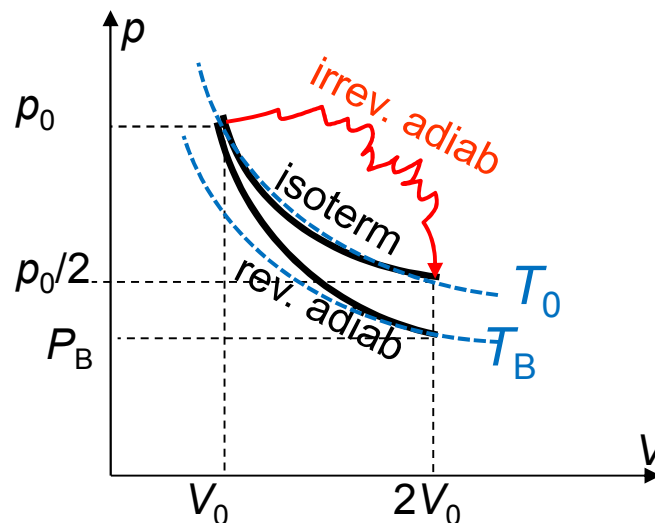
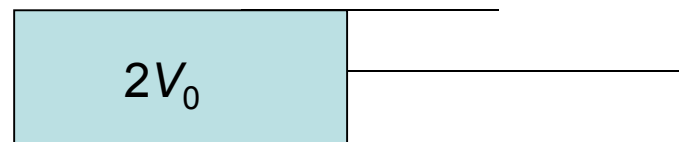


### Eks. 4. Reversibel adiabatisk utvidelse



reversibel adiabatisk  
 Temp. faller

$Q = 0$   
 $W > 0$   
 $\Delta U = Q - W < 0$   
 $\Delta S = 0$



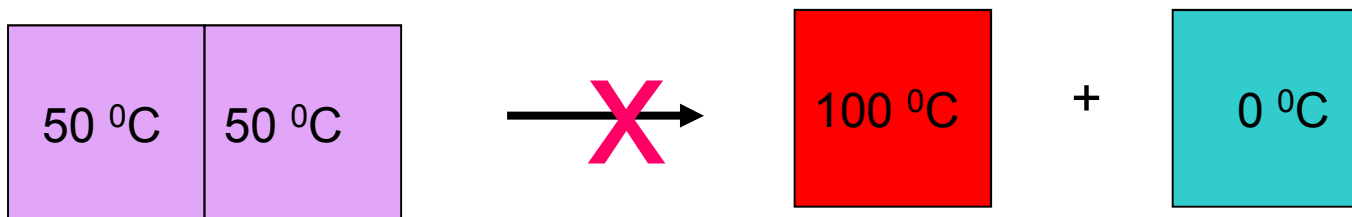
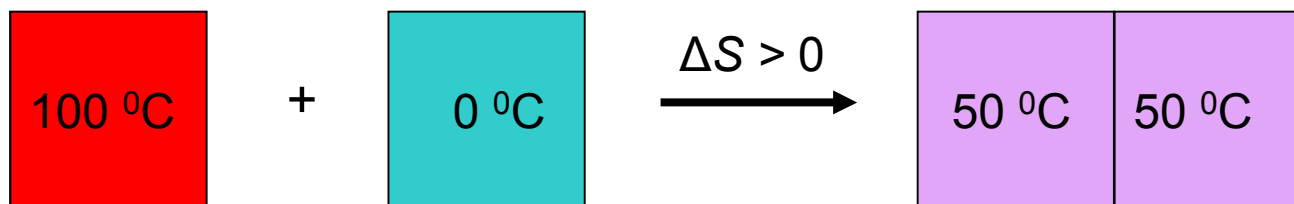
Id.gass:

$$S(T, V) = S_0(T_0, V_0) + nR \ln V/V_0 + nC_V \ln T/T_0 \quad (1A)$$

eller

$$S(p, V) = S_0(p_0, V_0) + nC_p \ln V/V_0 + nC_V \ln p/p_0 \quad (1B)$$

Entropien skal øke for denne prosessen, la oss beregne (Eks. 5)



Id.gass:

$$S(T,V) = S_0(T_0, V_0) + nR \ln V/V_0 + nC_V \ln T/T_0 \quad (1A)$$

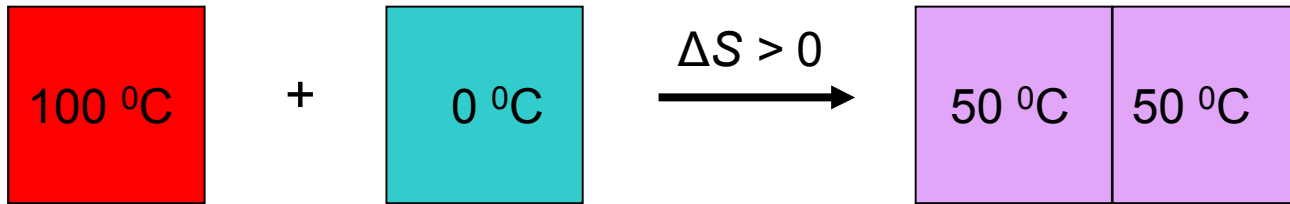
Ingen har observert varme strømme fra kaldt til varmt legeme

=>

Termodynamikkens 2. hovedsetning (én formulering)

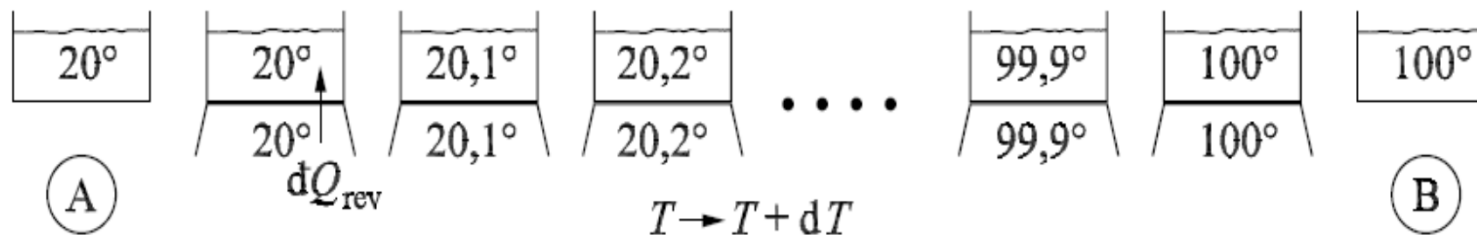
=>

$$\Delta S_{(\text{tot})} > 0 \text{ for spontane prosesser}$$

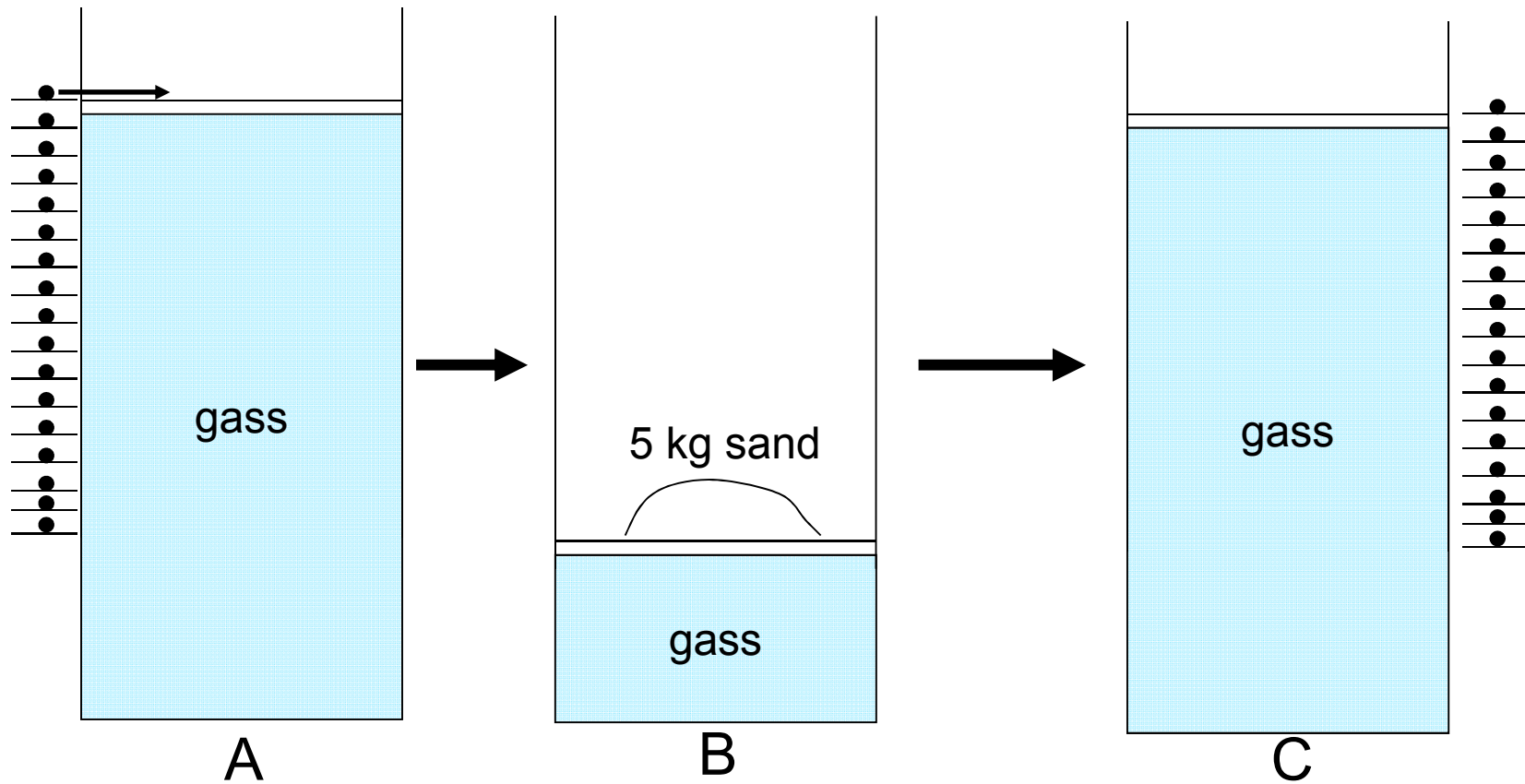


Øving 11, opg.3:

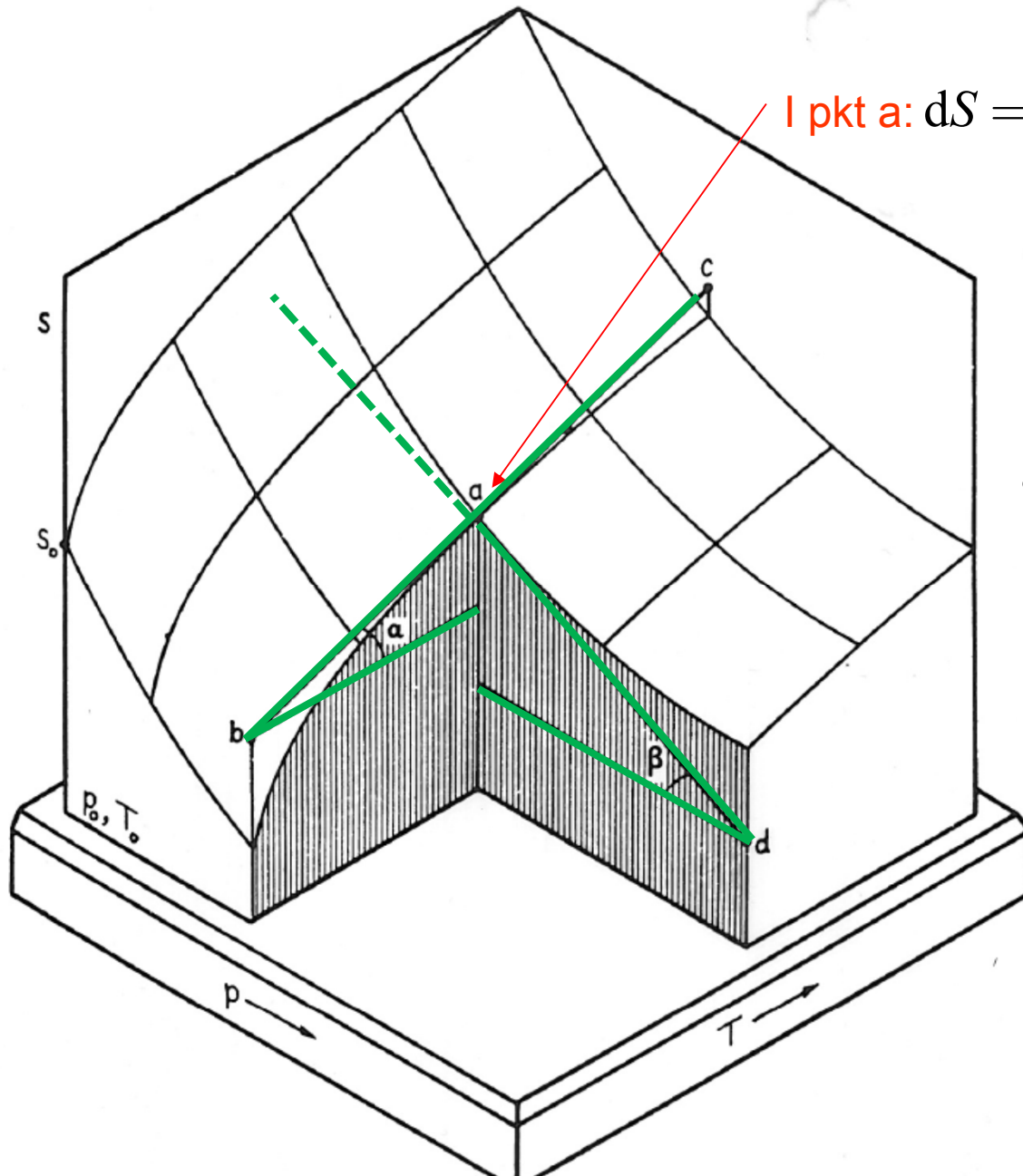
Oppvarming 20  $\rightarrow$  100 grader reversibelt  
ved uendelig mange varmereservoar:



**Uendelig mange varmereservoar er  
parallell til uendelig mange sandkorn:**



Entropi ideell gass:  $S(T,p) = S_0(T_0, p_0) + nC_p \ln T/T_0 - nR \ln p/p_0$  (1C)



I pkt a:  $dS = \left( \frac{\partial S}{\partial T} \right)_p dT + \left( \frac{\partial S}{\partial p} \right)_T dp$

$$= nC_p \frac{dT}{T} - nR \frac{dp}{p}$$

$$\alpha = \left( \frac{\partial S}{\partial T} \right)_p$$

$$\beta = \left( \frac{\partial S}{\partial p} \right)_T$$

Vanl.  
matem.

$$\frac{\partial S(T,p)}{\partial T}$$

→

Termo-  
dynamikk

$$\left( \frac{\partial S}{\partial T} \right)_p$$

Alle totale differensial for entropien S:

$$S(T, V) \Rightarrow dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV$$

Ideell gass:

$$S(T, V) = S_0 + nC_V \ln T/T_0 + nR \ln V/V_0 \quad (1A) \quad dS = nC_V \frac{dT}{T} + nR \frac{dV}{V}$$

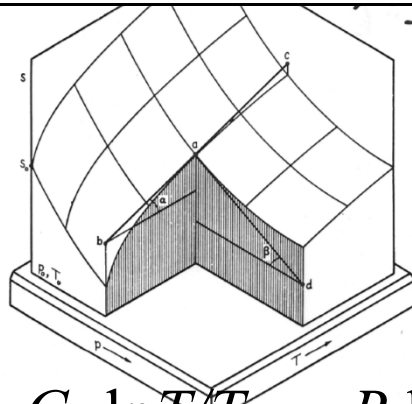

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$$S(p, V) \Rightarrow dS = \left( \frac{\partial S}{\partial V} \right)_p dV + \left( \frac{\partial S}{\partial p} \right)_V dp$$

Ideell gass:

$$S(p, V) = S_0 + nC_p \ln V/V_0 + nC_V \ln p/p_0 \quad (1B) \quad dS = nC_p \frac{dV}{V} + nC_V \frac{dp}{p}$$


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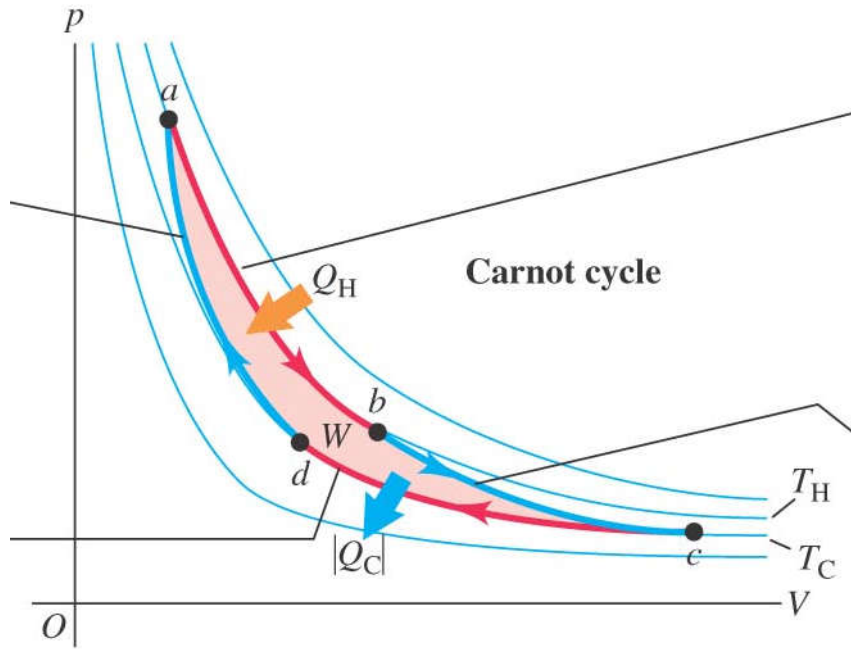
$$S(T, p) \Rightarrow dS = \left( \frac{\partial S}{\partial T} \right)_p dT + \left( \frac{\partial S}{\partial p} \right)_T dp$$

Ideell gass:

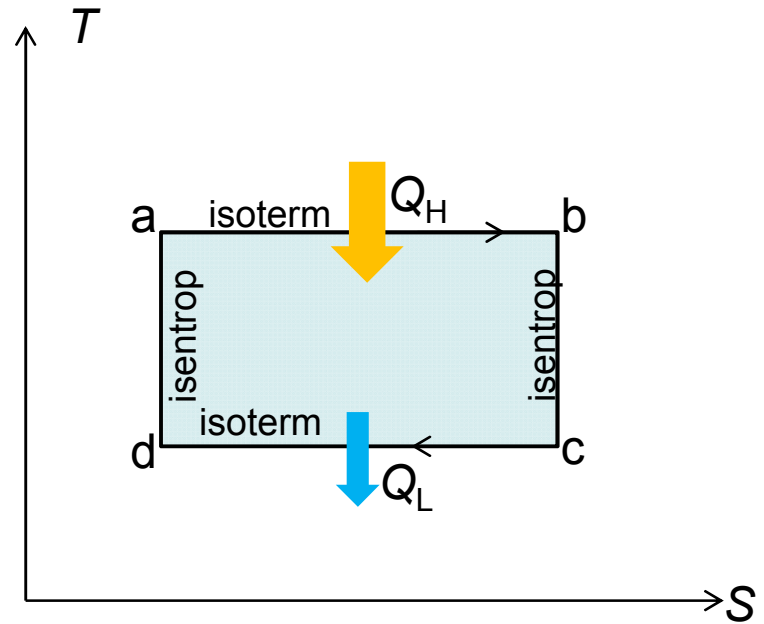
$$S(T, p) = S_0 + nC_p \ln T/T_0 - nR \ln p/p_0 \quad (1C) \quad dS = nC_p \frac{dT}{T} - nR \frac{dp}{p}$$



# Carnotsyklus:

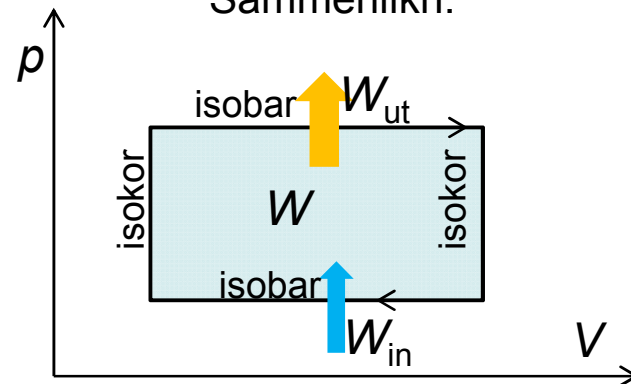


$pV$ -diagram:  
areal innenfor =  $\int p dV = W_{(netto)}$

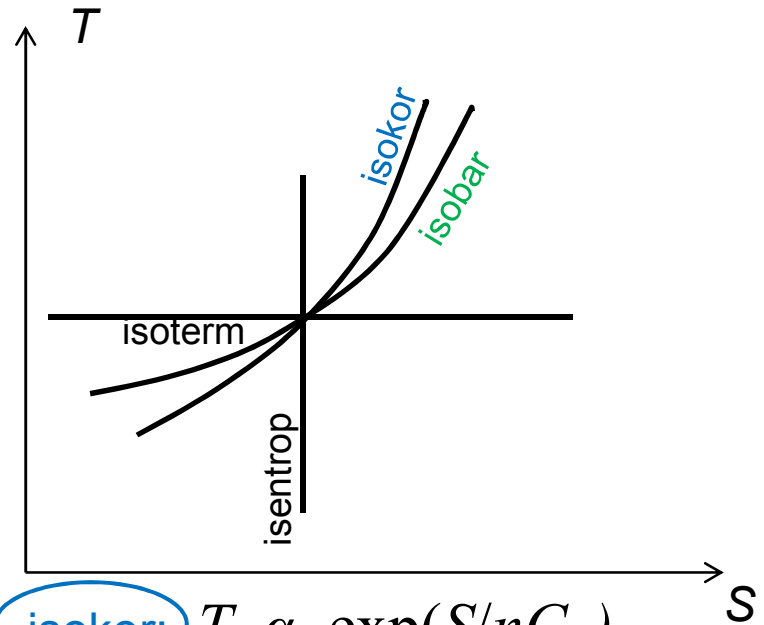
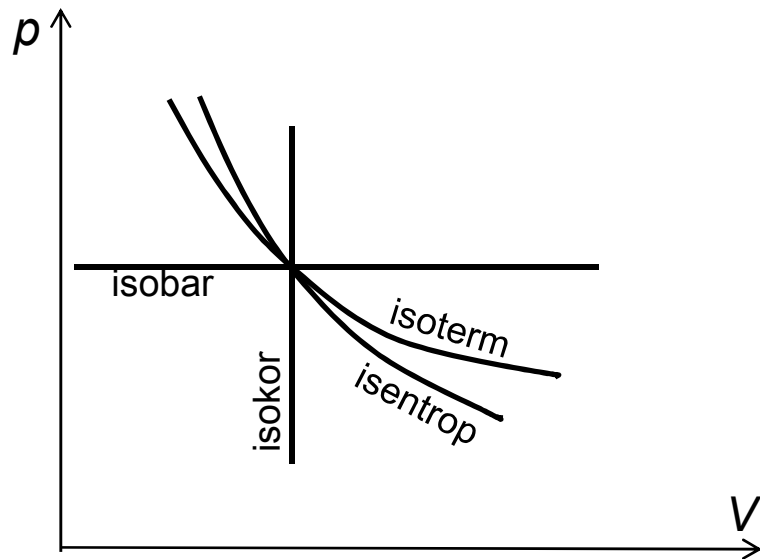


$TS$ -diagram:  
areal innenfor =  $\int T dS = Q_{(netto)}$

## Sammenlikn:



# Prosesskurver i $pV$ og i $TS$ -diagram (ideell gass):



isoterm:  $p \propto V^{-1}$

isentrop (adiabat):  $p \propto V^{-\gamma}$

isokor:  $T \propto \exp(S/nC_V)$

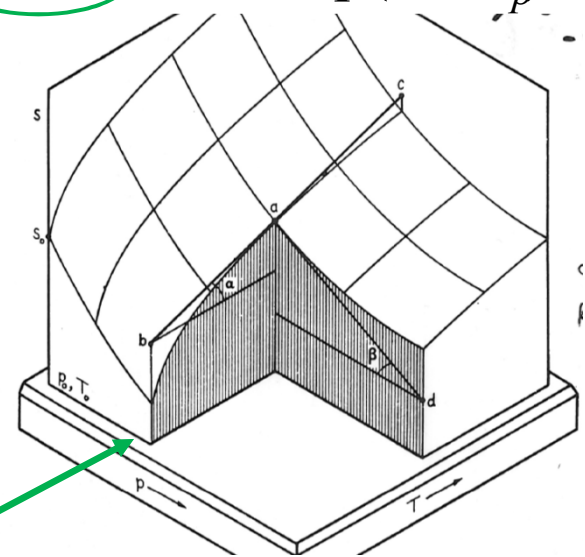
isobar:  $T \propto \exp(S/nC_p)$

$$S(T, V) = S_0 + nC_V \ln T/T_0 + nR \ln V/V_0 \quad (1A)$$

$V$  konst.

$$S(T, p) = S_0 + nC_p \ln T/T_0 - nR \ln p/p_0 \quad (1C)$$

$p$  konst.



# Entropien mikroskopisk

Kursorisk

[H&S 12.6, Y&F 20.8, L&H&L 17.11(deler av)]

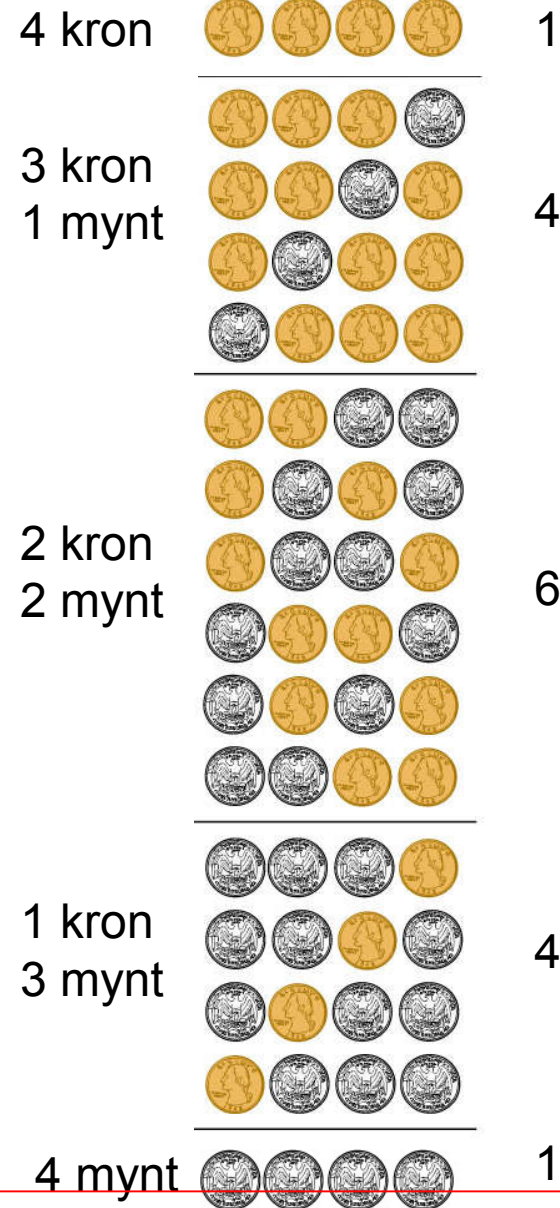
- $S$  uttrykk for systemets uorden, mer presist:  
 $S$  uttrykk for hvor mange mikroskopiske tilstander («mikrorot») en makroskopisk tilstand tillater:  
Større volum => flere tilstander:  $S \propto \ln V$   
Høyere  $T$  => flere hastighetsmuligheter:  $S \propto \ln T$
- Boltzmann:  $S = k_B \ln w$   
 $k_B$  = skaleringsfaktor = Boltzmanns konstant  
 $w$  = # mikrotilstander = termodynamisk sannsynlighet
- Spontan rydding er umulig:  
 $\Rightarrow \Delta S < 0$  umulig i spontane reaksjoner  
 $\Rightarrow S$  øker i lukka system
- Rydding krever arbeid:  
Tilført  $W$  kan redusere  $S$



Kron/mynt  
4 mynter:

Makroskopiske tilstander    Mikroskopiske tilstander, antall:


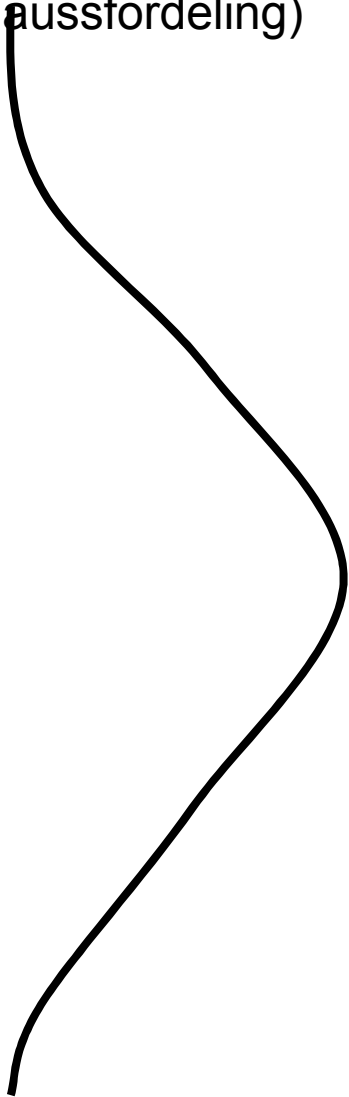








Mest sannsynlige makrotilstand (38 %)



Sum ant. tilstander: 5 makro     $2^4 = 16$  mikro

Y&F Figure 20.21

# Kron/mynt 8 mynter:

Makroskopiske tilstander	Mikroskopiske tilstander	antall:	(binomialformelen) (Gaussfordeling)
8 kron		1	
7 kron, 1 mynt		8	
6 kron, 2 mynt		28	
5 kron, 3 mynt		56	
4 kron, 4 mynt		70	
3 kron, 5 mynt		56	
2 kron, 6 mynt		28	
1 kron, 7 mynt		8	
8 mynt		1	

Mest sannsynlige makrotilstand

Y&F Figure 20.21

Sum ant. tilstander: 9 makro

$$w = 2^8 = 256 \text{ mikro}$$

Kron/mynt  
 $10^{24}$  mynter:

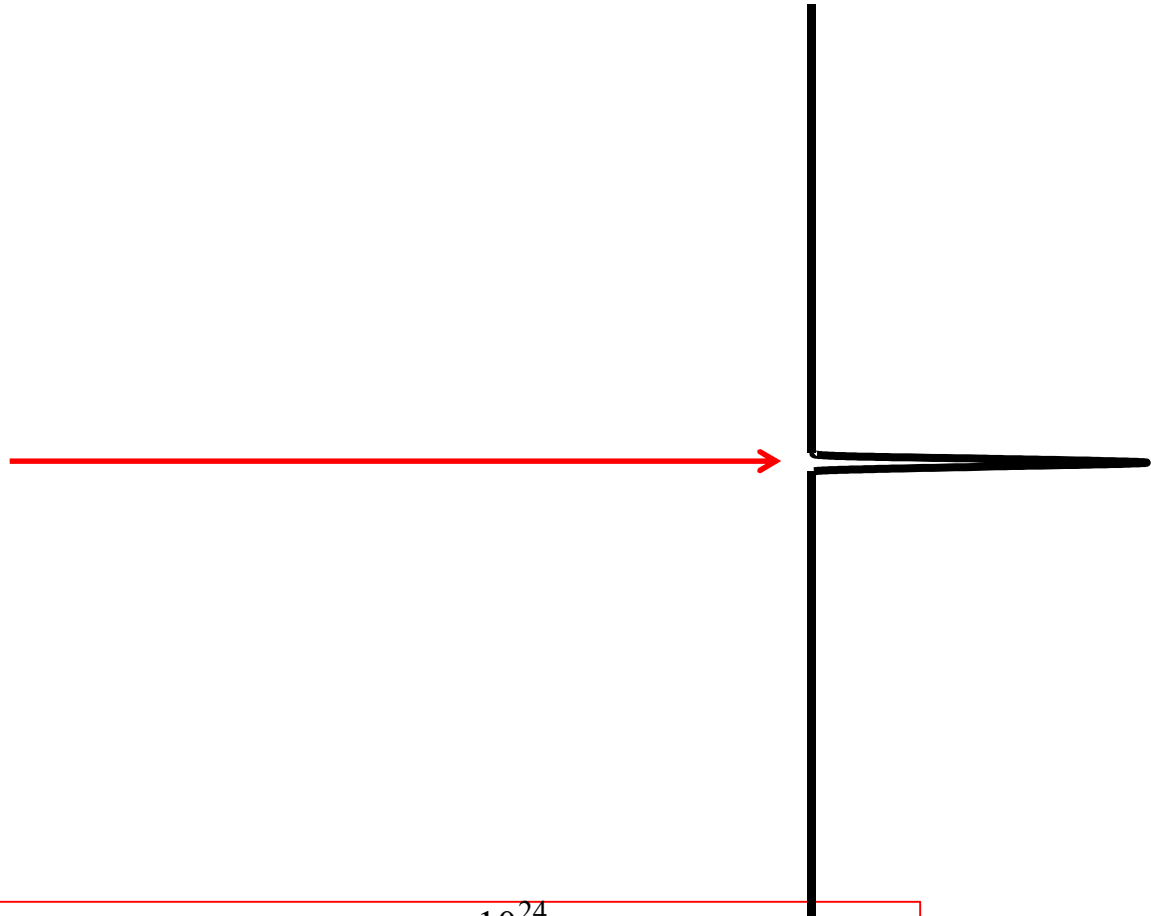
Gaussfordeling blir utrolig skarp ( $\delta$ -funksjon)

Mest sannsynlige makrotilstand = den eneste sannsynlige

Sum ant. tilstander: mikro:  $w = 2^{10^{24}}$  = uant stort tall

$\ln 2^{10^{24}} = 10^{24} \ln 2 =$  overkommelig tall

$k_B \ln w = k_B \ln 2^{10^{24}} = 1,38 \cdot 10^{-23} \cdot 10^{24} \ln 2 =$  «normal» størrelsesorden



# Antall mikrotilstander og dermed entropi øker med volumet

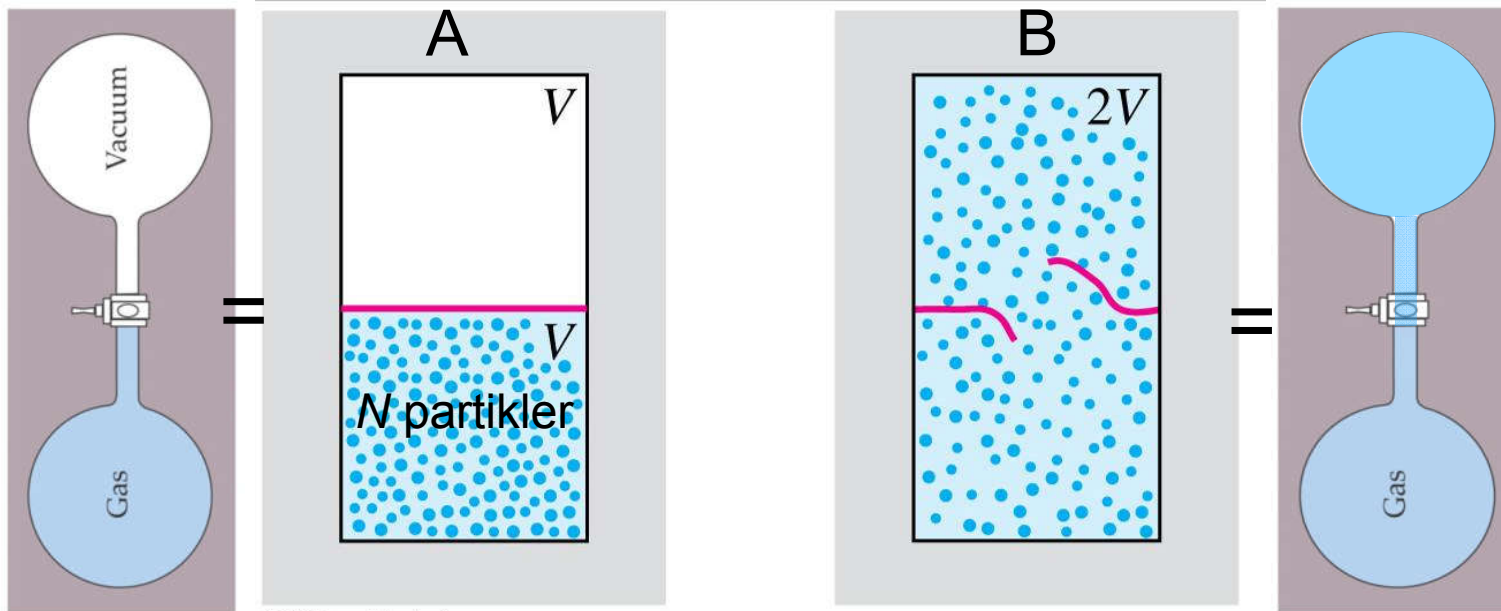
$$\# \text{ \mu tilstander} = w_1$$

$$\# \text{ \mu tilstander} = 2^N w_1 \gg w_1$$

$$S_A = k_B \ln w_1$$

$$S_B = k_B \ln 2^N w_1 = Nk_B \ln 2 + k_B \ln w_1$$

$$S_B - S_A = nR \ln 2$$



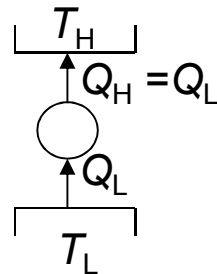
$\approx$  null sannsynlighet for at A opptrer

$$\text{Boltzmann: } S = k_B \ln w$$

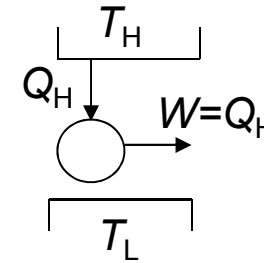
# Kap 20: Termodynamikkens 2. lov

## Oppsummert

2. lov, Clausius: UMULIG:



2. lov, Kelvin: UMULIG:



Carnotprosess:

Kretsprosess med to isotermer og to adiabatener,  
 eneste mulige reversible prosess mellom kun to varmereservoar.

Carnots teorem:

1. Uansett arbeidssubstans er for Carnotprosess:  $\eta_C = 1 - T_L/T_H$
2. Ingen kretsprosess mellom to reservoarer kan ha større  $\eta$  enn  $\eta_C$

Clausius' (u)likhet for kretsprosesser:

$$\int dQ/T = 0 \quad \text{reversibel kretsprosess} \quad \int dQ/T < 0 \quad \text{irreversibel kretsprosess}$$

Def. entropi:  $dS = dQ_{\text{rev}}/T$  eller  $\Delta S = \int dQ_{\text{rev}}/T$

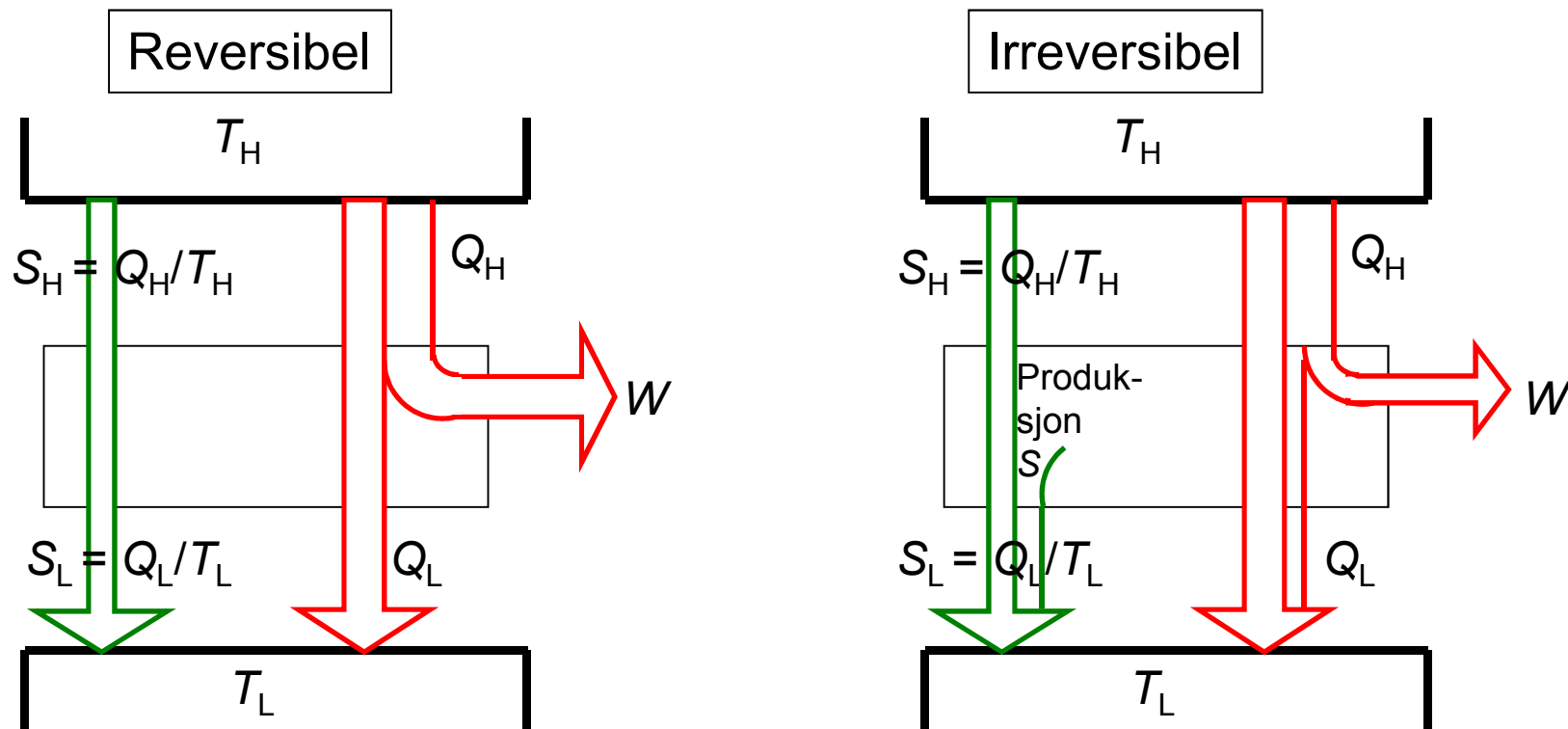
$S$  er tilstandsfunksjon, ikke avhengig vegen. Beregning må gjøres via rev. prosess, men resultatet er det samme uansett, når start- og slutttilstand er gitt

For ideell gass:  $S(T, V) = S_0(T_0, V_0) + nR \ln V/V_0 + nC_V \ln T/T_0$ , samt  $S(T, p)$  og  $S(p, V)$

For lukket system (og for universet) kan ikke entropien avta i en prosess.  
 Entropien et mål for mikroskopisk rot i et makroskopisk system.

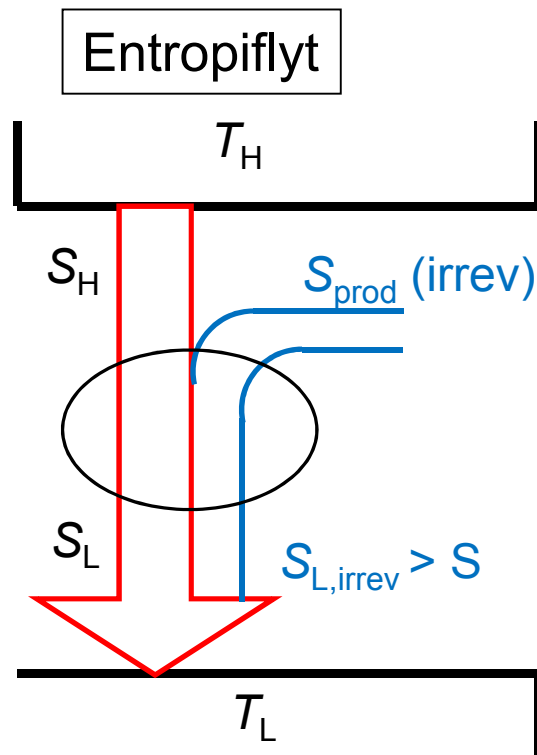


# Varmekraftmaskin mellom to varmereservoar Energiflyt og entropiflyt.

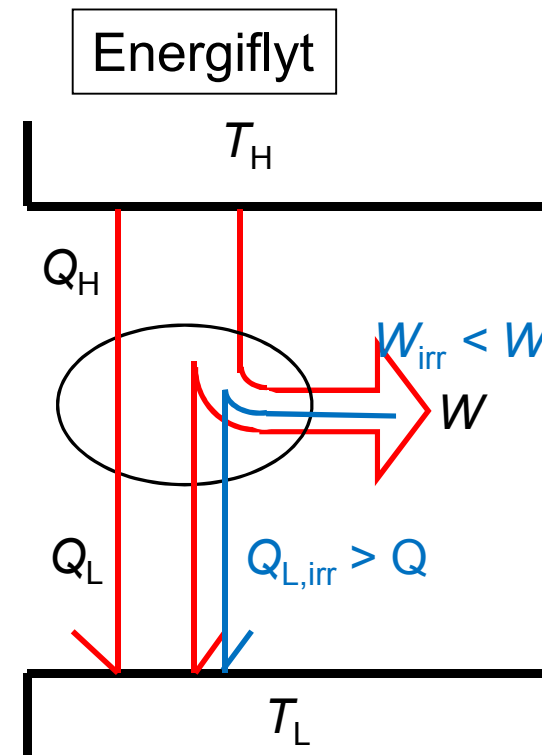


For å fjerne entropiproduksjon må  $Q_L = S_L T_L$  være større, dermed  $W$  mindre.  
 $\eta = W/Q_H$  avtar

# Varmekraftmaskin mellom to varmereservoar



**Reversibel maskin**  
Enhver irreversibilitet  
i maskinen produserer entropi  $S_{\text{prod}}$ ,  
som må fjernes fra maskinen.



**Reversibel maskin**  
Fjerning av  $S_{\text{prod}}$  gjennom  $Q_L$   
 $\Rightarrow Q_L$  må økes  
og  $W$  må reduseres,  
 $\eta = W/Q_H$  avtar.

# Hva er rett og hva er galt?

$$\int_1^2 dU = U_2 - U_1 \quad \text{OK}$$

$$\int_1^2 dW = W_2 - W_1 \quad \text{feil}$$

$$U(T, V) \quad \text{OK}$$

$$Q(T, V) \quad \text{feil}$$

$$\int_1^2 dW = \int_1^2 p dV = p \Delta V \quad \begin{array}{l} \text{Første "=" OK;} \\ \text{siste "=" OK i isobar prosess} \end{array}$$

$$\int_1^2 dQ = \int_1^2 T dS = T \Delta S \quad \begin{array}{l} \text{Første "=" OK i reversibel prosess;} \\ \text{siste "=" OK i isoterm prosess} \end{array}$$

$$dU = \overset{\color{red}{\cancel{d}}}{d}Q - \overset{\color{red}{\cancel{d}}}{d}W \quad \text{OK med «d-strek»}$$

$$dU = T dS - p dV \quad \text{OK reversibel prosess}$$

# Energier (potensialer, tilstandsfunksjoner) i termodynamikken

Indre energi («grunnenergien»):

$U$  = total indre energi

$$dU = TdS - p dV \quad (= 1. \text{ hovedsetning})$$

$$\text{isokor: } dU = T ds = \overset{+}{d}Q \quad \Rightarrow C_V = (dU/dT)_V$$

Entalpi:

--- varme når konst. trykk

$$H(S,p) = U + pV$$

$$dH = T dS + V dp$$

$$\text{isobar: } dH = T dS = \overset{+}{d}Q \quad \Rightarrow C_p = (dH/dT)_p$$

Helmoltz fri energi:

$$F(T,V) = U - TS$$

$$dF = - S dT - p dV$$

Gibbs fri energi:

--- viktig for likevektsbetingelser

$$G(T,p) = U + pV - TS$$

$$dG = - S dT + V dp$$

Ikke tid for disse  
i TFY4115