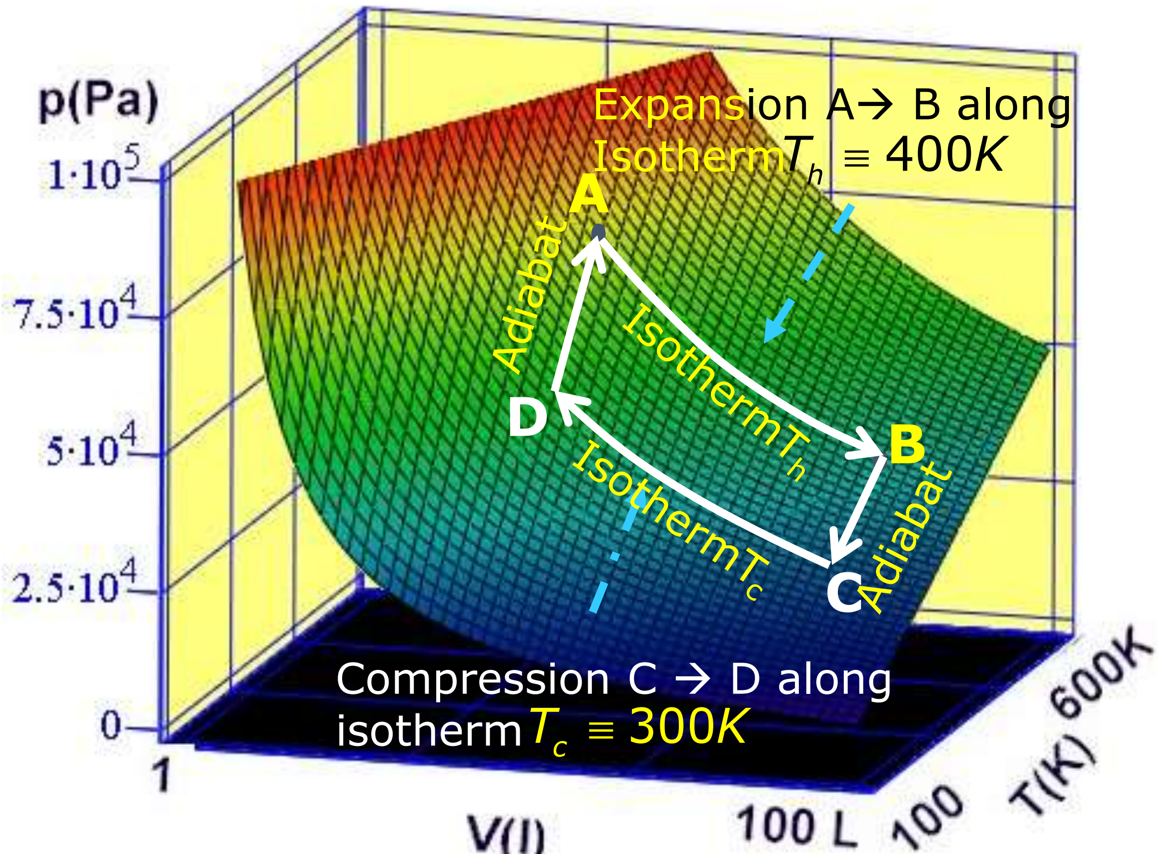
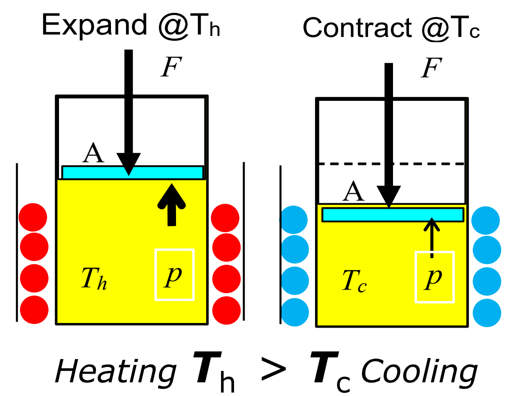
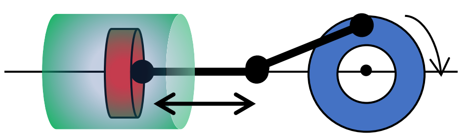
Reversible Circular Processes on EoS Hyperplane

$$\underbrace{P \cdot V = R \cdot T}_{\text{For } T = const.} \quad \text{OR} \quad \underbrace{P \cdot V^{\gamma} = const;\ T \cdot V^{\gamma-1} = const}_{\text{For } q = 0}$$

Circular, reversible process
A→B→C→D→A
on the EoS hyperplane







returns the IG system to its initial state A after a combination of slow (=reversible) expansion and compression processes.

Ideal Gas Constant *R*

R = 0.0821 liter·atm/mol·K

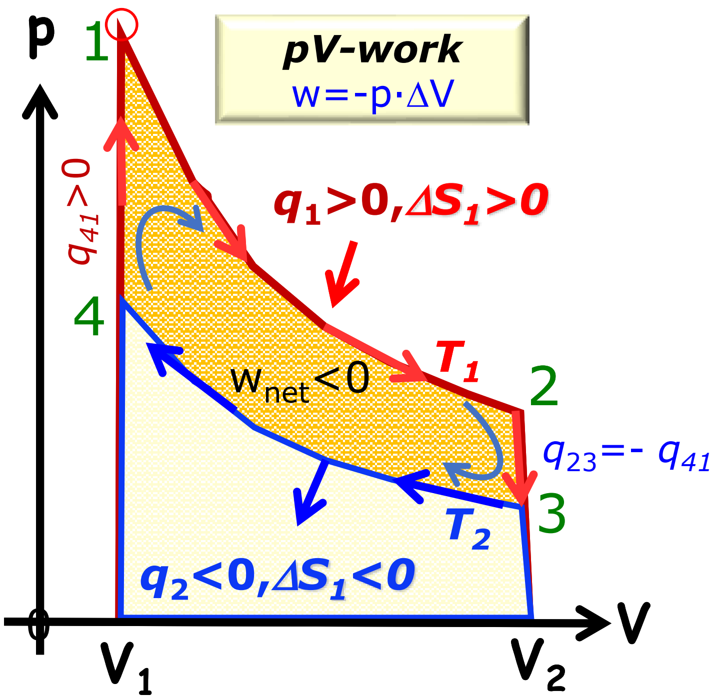
R = 8.3145 J/mol·K

Heat and cool the working IG volume @ specific times → Cyclic thermal engine

Thermal Engine with ***Ideal*** Working Medium

Ideal-gas system (N particles) in alternating contact with Heat Bath @ T_1 and Cold Sink @ $T_2 < T_1$

$$EoS: p \cdot V = N \cdot k_B \cdot T$$



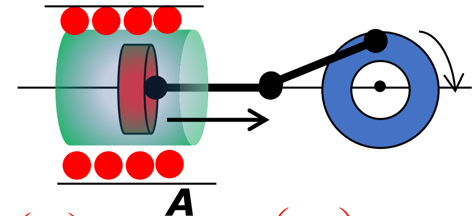
Isochoric legs: No net heat transfer→ no change net ΔS

Heat energy transfer

$$q_i = (T \cdot \Delta S)_i \,;\, \Delta S = |\Delta S_i|$$

1→2 Isothermal expansion @T_1=const

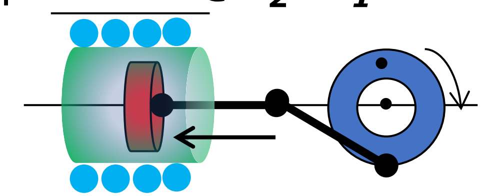
$$w_1 = -\int_{V_1}^{V_2} p(V,T)\,dV = Nk_BT_1 \cdot Ln(V_1/V_2)$$



$$\frac{w_1}{T_1} = Nk_BLn\left(\frac{V_1}{V_2}\right) = \frac{-q_1}{T_1} \to \left(\frac{q}{T}\right)_1 = Nk_BLn\left(\frac{V_2}{V_1}\right) = \Delta S_1$$

3→4 Isothermal compression @$T_2<T_1$

$$w_2 = -\int_{V_2}^{V_1} p(V,T)\,dV = -Nk_BT_2 \cdot Ln(V_1/V_2)$$



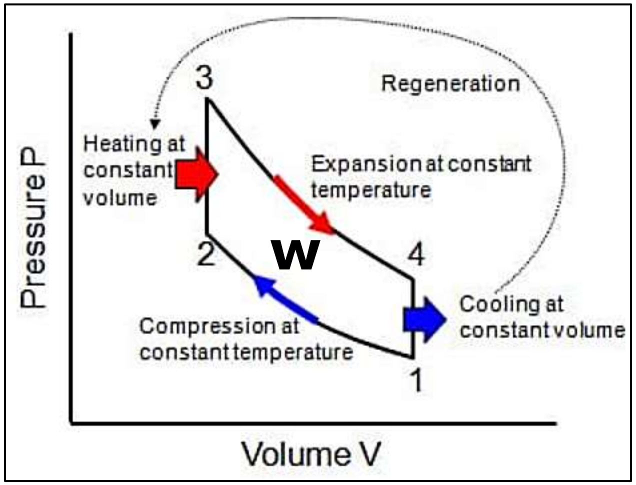
$$\frac{w_2}{T_2} = Nk_BLn\left(\frac{V_2}{V_1}\right) = \frac{-q_2}{T_2} \to \left(\frac{q}{T}\right)_2 = Nk_BLn\left(\frac{V_1}{V_2}\right) = \Delta S_2$$

$$\Delta S_1 = -\Delta S_2 \equiv \Delta S$$

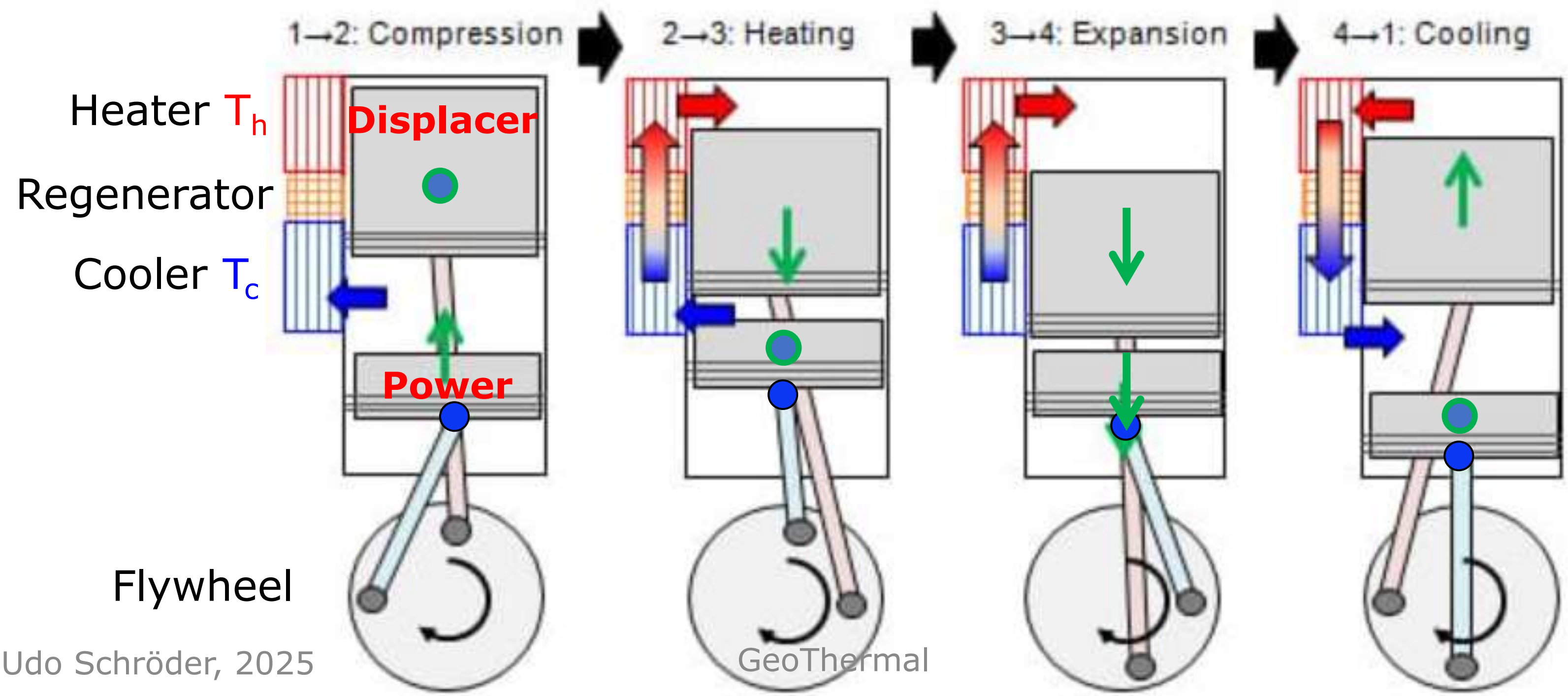
Cyclic path conserves S(1)

Entropy=State Fcn

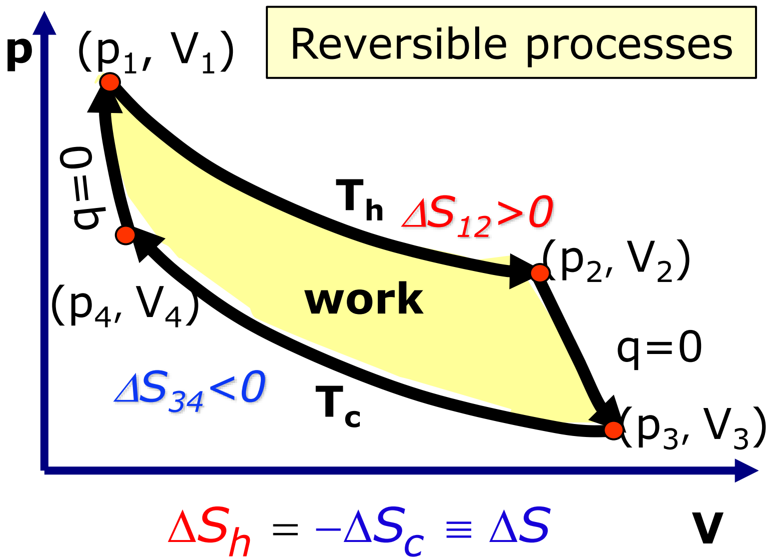
Stirling Heat Engine (β)

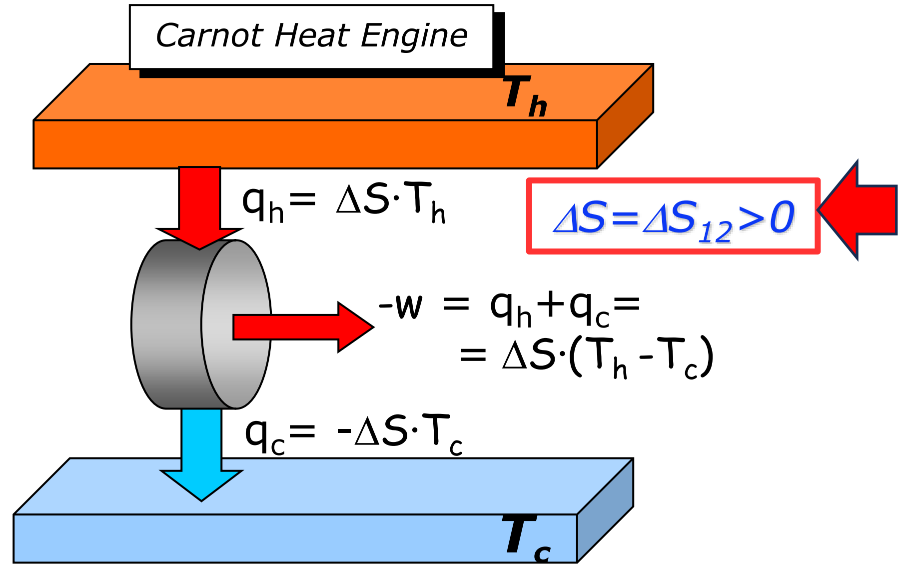


Closed-cycle regenerative heat engine with self-contained, permanent working fluid/gas. Displacer directs flow of working gas between hot and cold spaces.
Stirling engine driven by ***T*** gradient, e.g., solar radiation, nuclear decay heat.
Applications: concentrated solar insolation, submarines, space craft,..



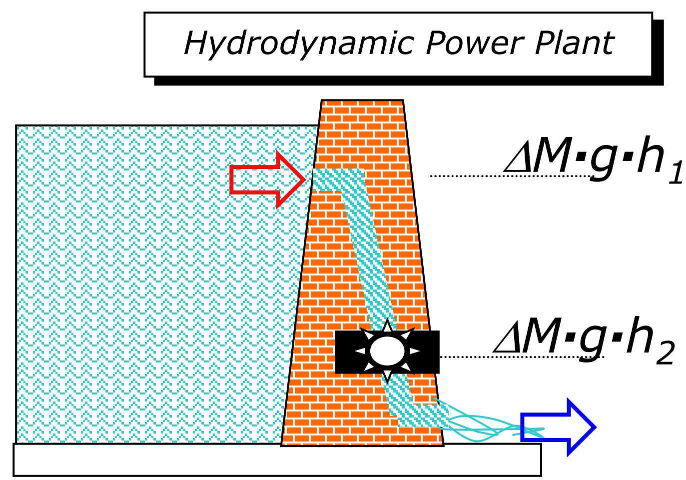
Entropy Flow in Carnot Engines





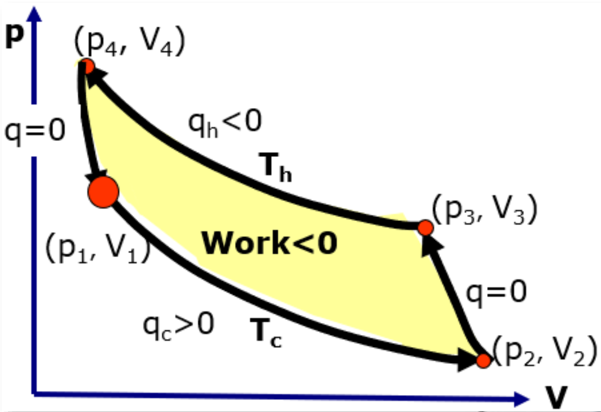
$$\varepsilon = \frac{-w}{q_h} = \frac{q_h + q_c}{q_h}$$

$$\varepsilon = 1 + \frac{q_c}{q_h} = 1 - \frac{T_c}{T_h} \xrightarrow[T_h \to \infty]{} 1$$



Water stream from reservoir carries energy driving an electric generator.

Residential Heat Pump

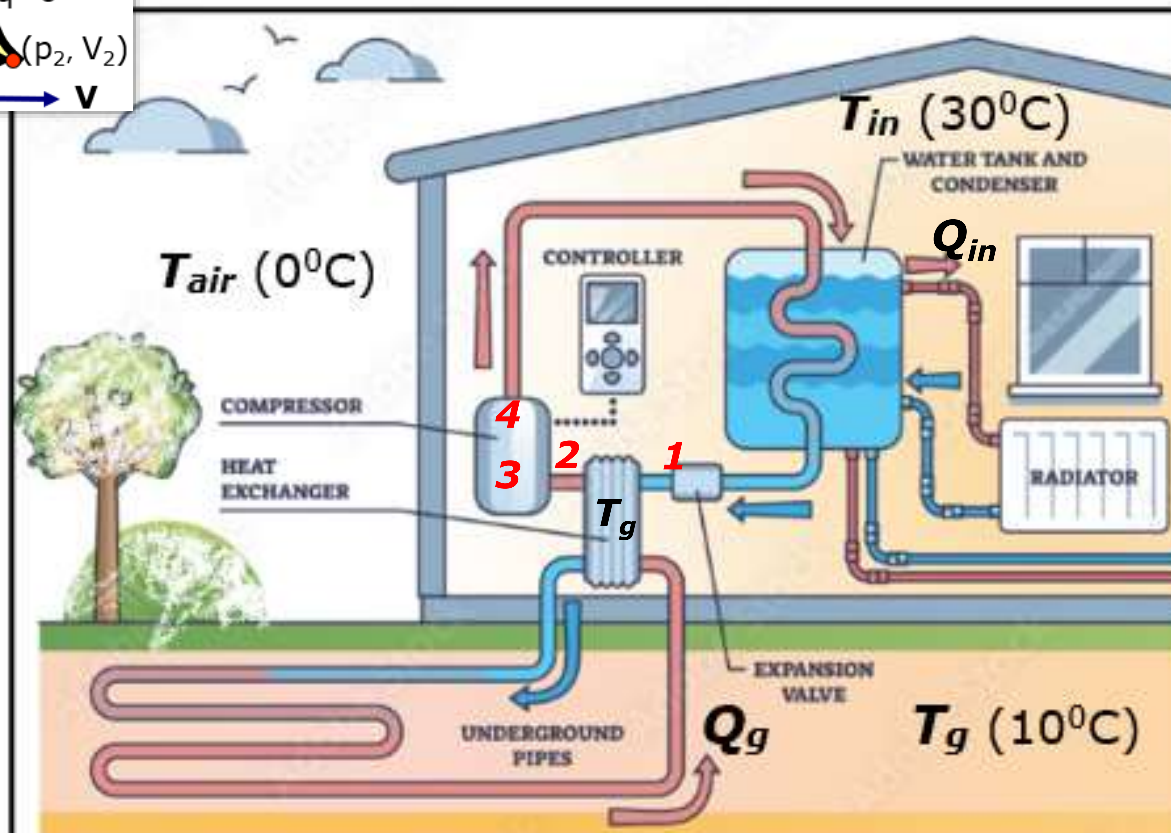


Carnot heating: In-ground heat pump absorbs heat energy $\boldsymbol{Q_g \approx \Delta S \cdot T_g}$ from under ground $\boldsymbol{T_g}$ heat bath to preheat expanded work fluid/gas. Compressor provides differential heat $\boldsymbol{Q_{in} \approx -\Delta S \cdot T_{in}}$ required for sustaining temperature $\boldsymbol{T_{in}}$.

Work fluid transfers heat $\boldsymbol{Q_{in} < 0}$ to tank and interior. Iso-thermal expansion after expansion nozzle in ground loop heat exchanger.

Req. compressor work

$$w = C_{air} \cdot \left(T_{in} - T_{air}\right) - \left|Q_g\right|$$



Thermal Power Plants

Agenda: Thermal Power Plants

- Operational principle of cyclic thermodynamic engines
  - Entropy, heat, and work in Carnot cycle
- Reciprocating (piston) engines
  - Steam cylinder
  - Otto internal combustion cycle
  - Stirling engine
- Steam power plants
  - Isotherms of real gases
  - Steam and air as working media
  - S-T cycles for Carnot, Rankine, and Brayton cycles
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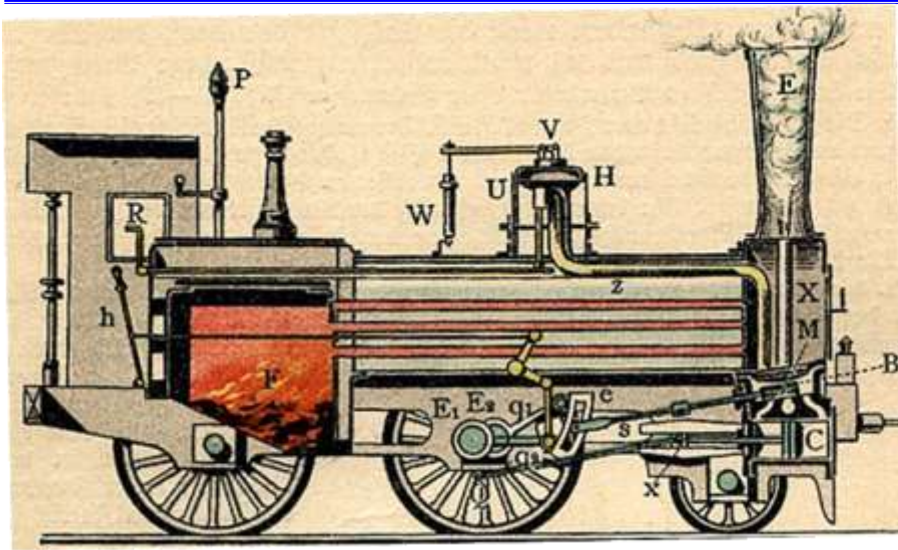
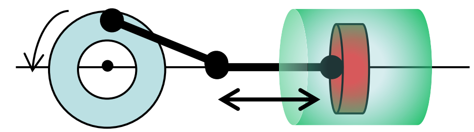
- Carbon (CO_2) capture processes

Next: Power from nuclear transmutation
Andrew & Jelley Chs. 9 & 10

Uniflow Steam Cylinder



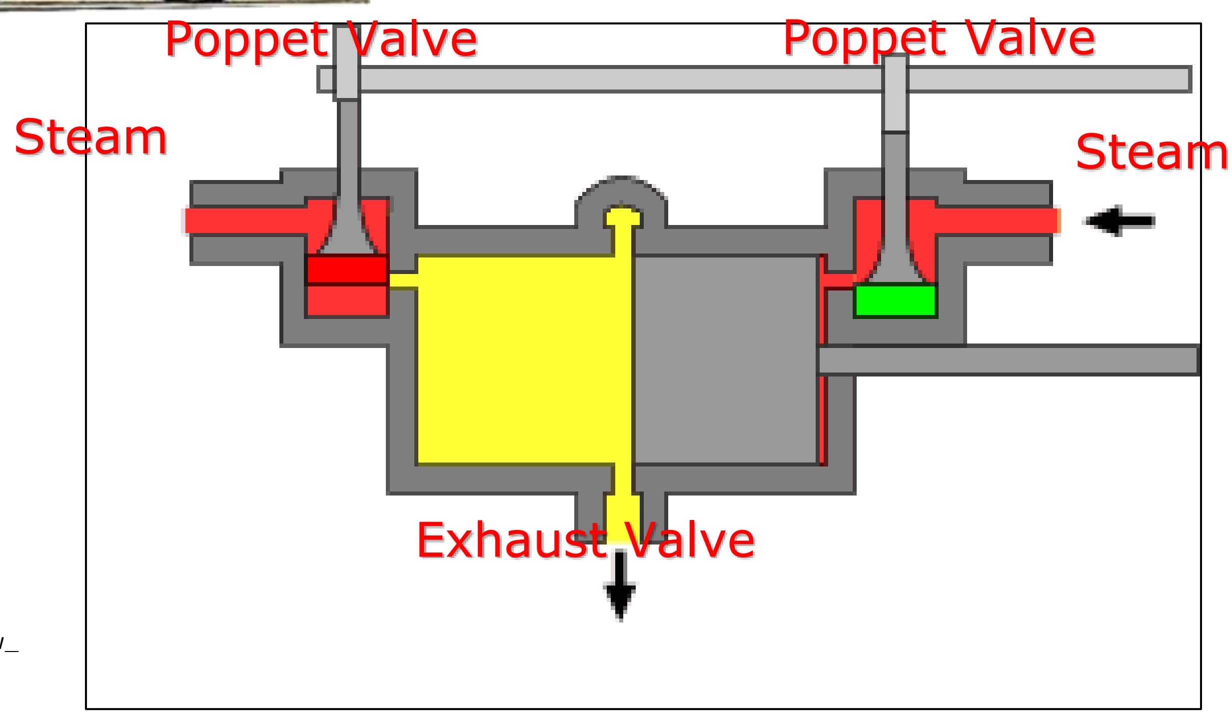
Linear motion is converted via excentric lever on crank wheel. produced by geared rotational motion, sustained by inertia.



Poppet valves connected to piston via levers or rotating crank shaft steer steam inlet and exhaust outlet.

Red = path closed
Green= path open

https://commons.wikimedia.org/wiki/File:Uniflow_steam_engine.gif



Early Steam Engines (America's Centennial Exposition 1876)

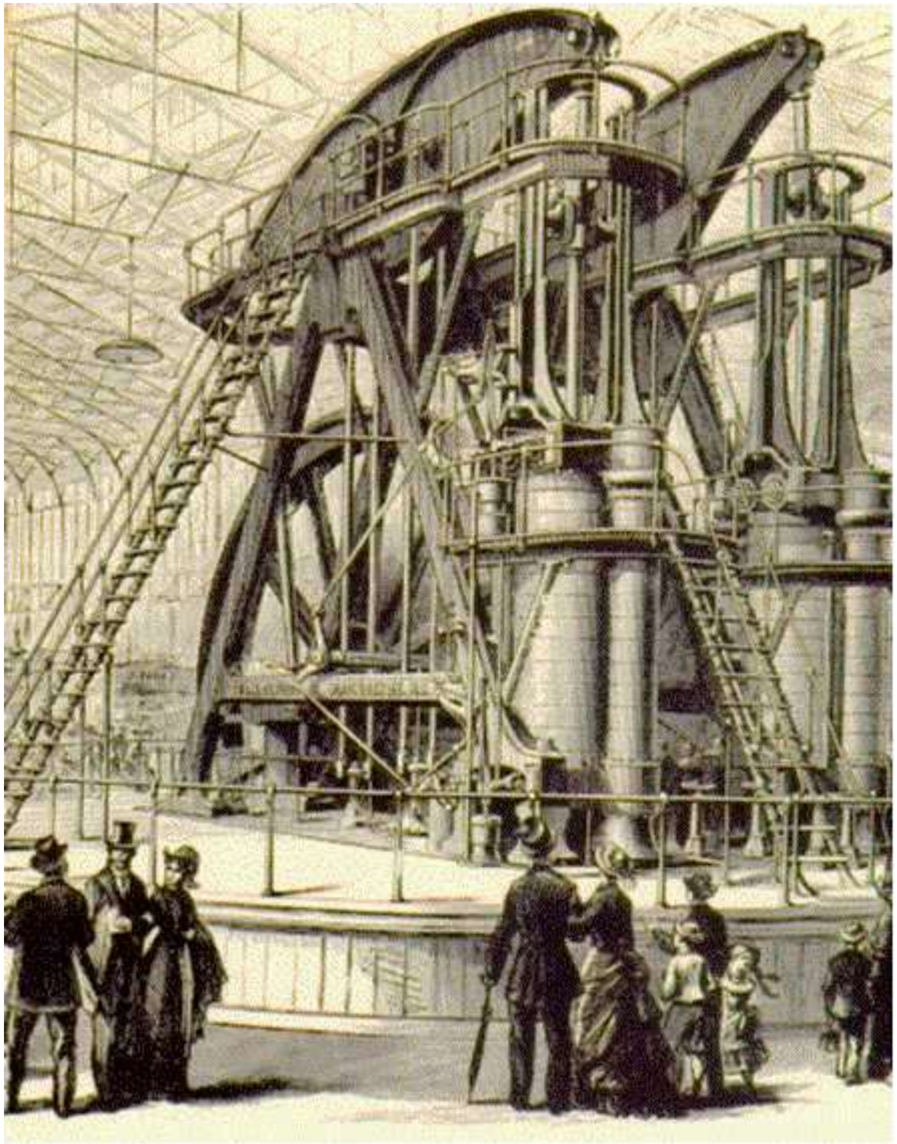
George H. Corliss.
Inventor, Providence, RI

American made Corliss steam engine at the Philadelphia exhibition.

Eye witness account:
"It stood in excess of forty-five feet above the floor and has cylinders of forty-four inches in diameter with a ten foot stroke. Another characteristic is the huge fifty-six ton, thirty feet in diameter, and twenty-four inch face, flywheel which made up to thirty-six revolutions per minute." (McCabe)

America's Centennial Exposition, →→→
held in Philadelphia in 1876

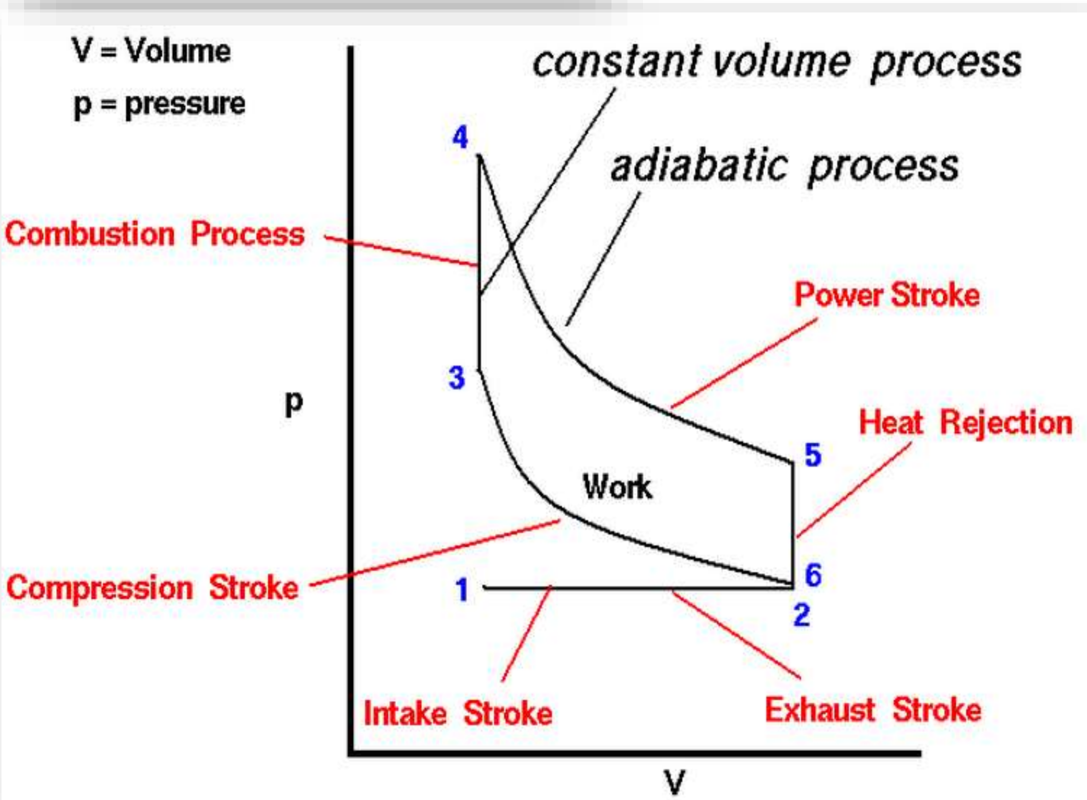
The pictured steam engine powered all machines and devices in the exhibition. It was operated by a single engineer. W=1,400 hp

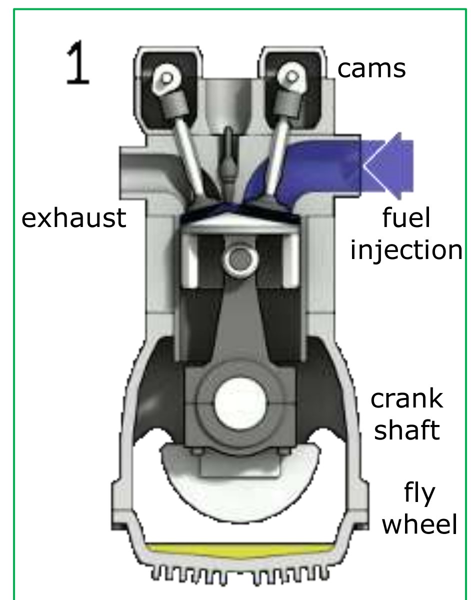


Ideal Otto Cycle

1) Intake stroke (1→2), gasoline vapor and air drawn into engine.
2) Compression stroke (2→3) . *p,T* increase.
3) Combustion (spark) (3→4), short time, *V*= constant. Heat absorbed from high-*T* "reservoir".
4) Power stroke: expansion (4→5).
5) Valve exhaust: Valve opens, gas can escape.
6) Emission of heat (5→6) to *low-T reservoir.*
7) Exhaust stroke (2→1), piston evacuates cylinder.

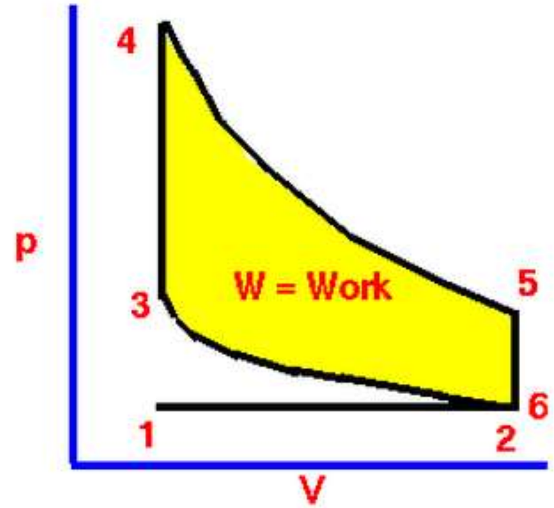
Needs engine starter !





Energetics of Otto Cycle

C_v = Specific Heat constant volume
γ = Specific Heat Ratio C_p/C_V
p = pressure
T = Temperature
V = Volume
f = fuel / air ratio
Q = Fuel heating value
c p s = cycles per second
P = Power
V_2/V_3 = r = Compression Ratio



Compression Stroke:
$T_3/T_2 = r^{\gamma-1}$
$p_3/p_2 = r^{\gamma}$

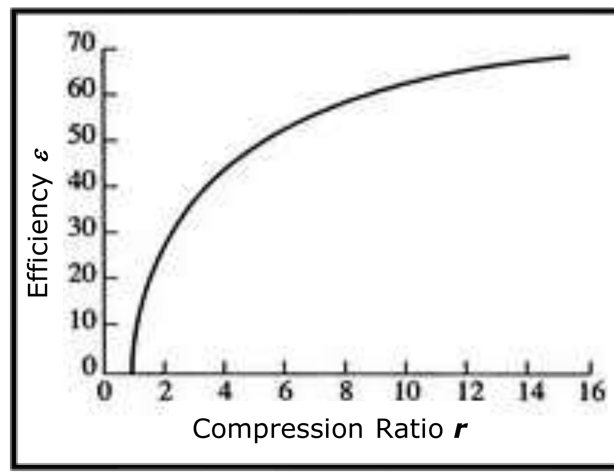
Combustion:
$T_4 = T_3 + fQ/c_V$
$p_4 = p_3(T_4/T_3)$

Power Stroke:
$T_5/T_4 = r^{1-\gamma}$
$p_5/p_4 = r^{-\gamma}$

$$Efficiency: \varepsilon = \frac{w}{q_{3\to4}} = \frac{q_{3\to4}+q_{5\to6}}{q_{3\to4}} = \frac{c_V\left(T_4-T_3\right)+c_V\left(T_6-T_5\right)}{c_V\left(T_4-T_3\right)}$$

$$\varepsilon = 1-\frac{\left(T_5-T_6\right)}{\left(T_4-T_3\right)}$$

$$Adiabatic\ EoS\left[T\cdot V^{R/c_V}=const.\right]\rightarrow \boxed{\varepsilon = 1-r^{-R/c_V}}$$



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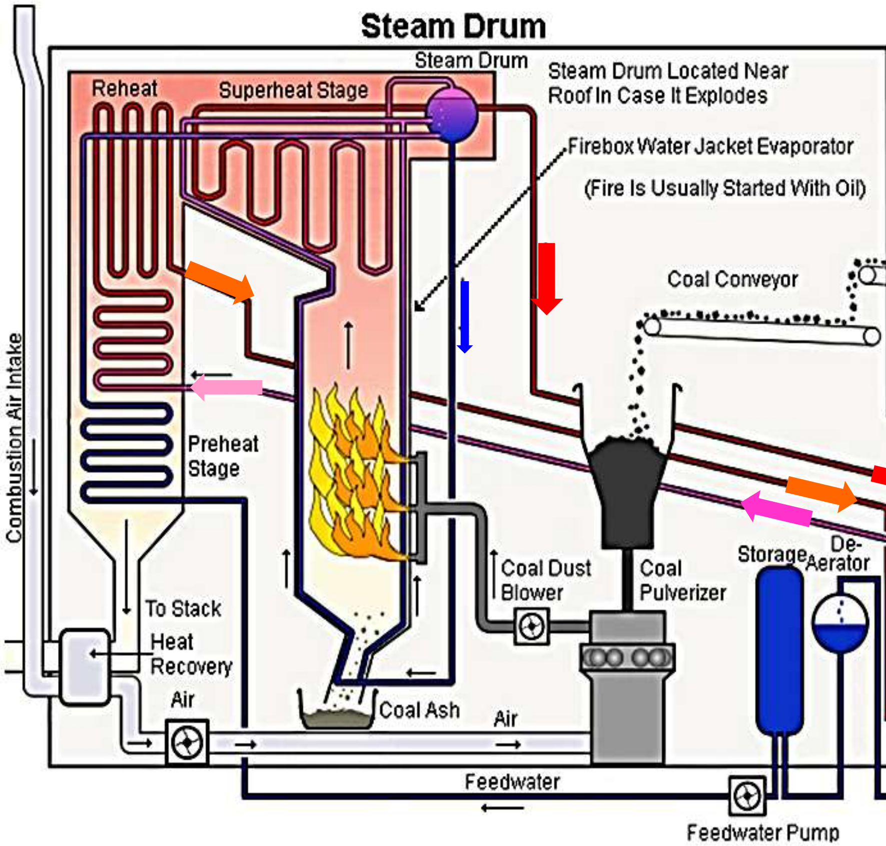
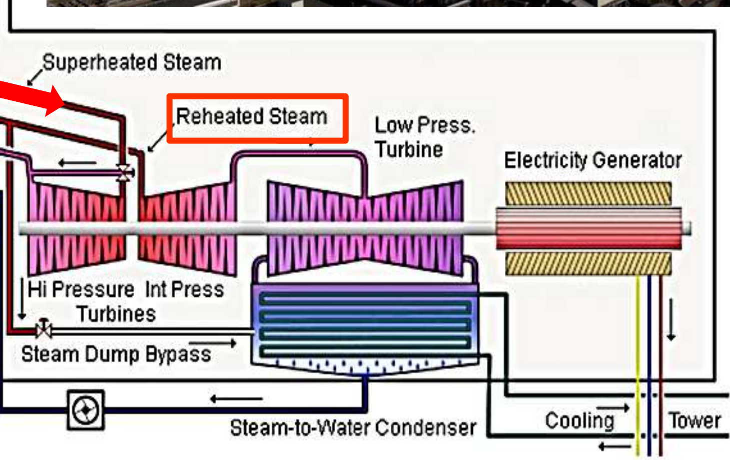
Andrew & Jelley Chs. 9 & 10

Coal Power Plant (Photo & Schematic)

Modern coal power plant: 3-7 GW_{th}. Two turbines in tandem working with reheated steam. Practical for *T<700 ⁰C.*





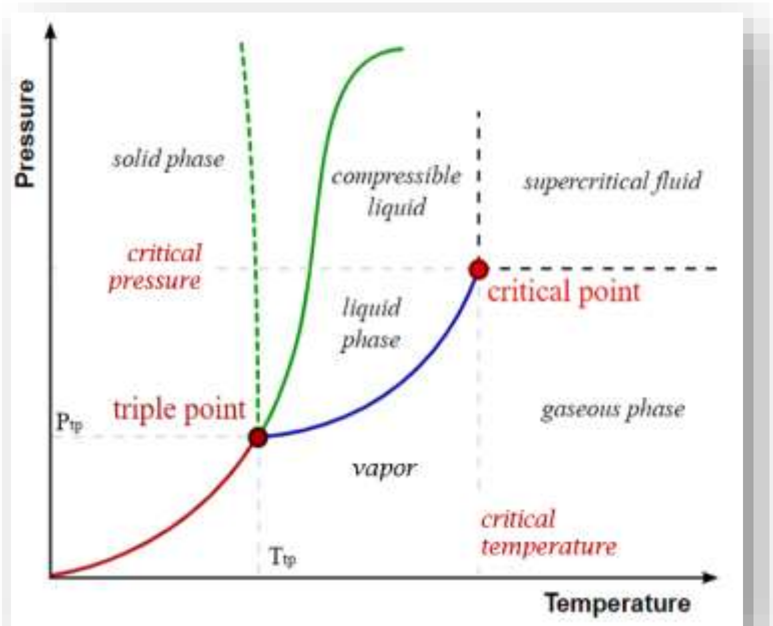
Real Substances (Different Phases: *s*, *ℓ*, *g*, *sc*)

All real substances have distinct physical phases:

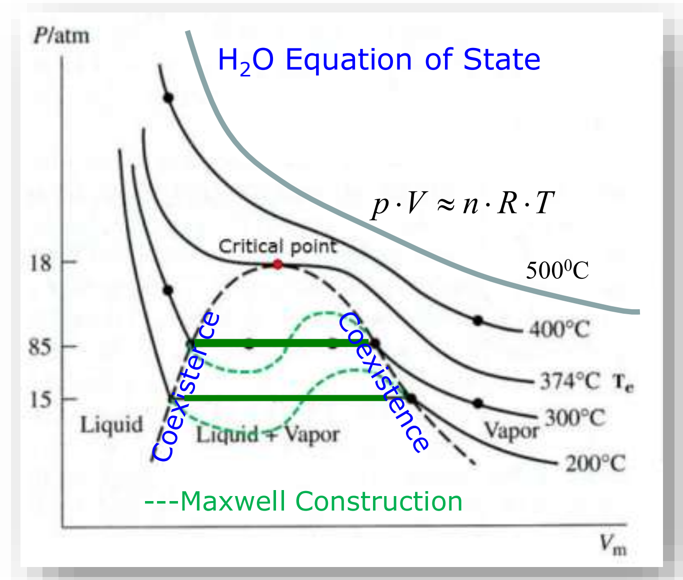
solid ($T<T_{freeze}$), liquid ($T_{freeze}<T<T_{boil}$) and gas ($T_{boil}<T$)

Phase transitions occur upon changes in internal energy by characteristic amounts: *latent heat* (*Δ-enthalpy*) *of fusion or latent heat of vaporization*

$$Enthalpy\ \boxed{H = U + P_{ext} \cdot V_{sys}} \qquad at\ P_{ext} : q = \Delta H = C_p \Delta T;\ heat\ capacity\ C_p$$



		Critical pressure P_c		Critical temperature T_c		
Material	Formula	psia	bar (abs)	°F	°C	$k = C_p/C_v$
Water	H_2O	3206	221	705	374	1.32



----*van der Waals gas model*

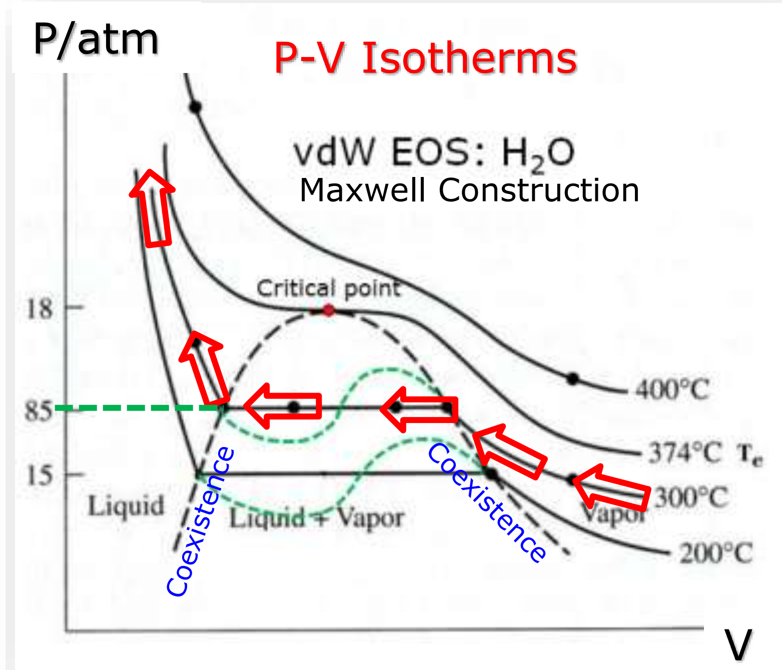
$$\left(p + \frac{n^2 \cdot a}{V^2}\right) \cdot (V - n \cdot b) = n \cdot R \cdot T$$

Using Real Gases/Vapor Working Media

Since 150 years practical use: steam = water vapor, water droplets (wet steam).
→ Real gas molecules interact more, motion is less free, depending on ρ, T.
→ Several phases.

$$\text{Ideal – Gas EoS } p \cdot V = R \cdot T \text{ (per mole)} \rightarrow$$
Virial expansion of compression factor

$$\mathbf{z} = \frac{p \cdot V}{R \cdot T} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \ldots =: \sum_{n=0}^{\infty} \frac{c_n(T)}{V^n}$$



Useful Parameterizations

van der Waals EoS:
$$p = \frac{n \cdot R \cdot T}{(V - n \cdot b)} - \frac{n^2 \cdot a}{V^2}$$

Redlich Kwong EoS:
$$p = \frac{n \cdot R \cdot T}{(V - nb)} - \frac{n^2 a}{\sqrt{T}} \cdot \frac{1}{V(V + nb)}$$

Van der Waals Parameters

Substance	a (L^2 atm/mol^2)	b (L/mol)
He	0.0341	0.0237
H_2	0.244	0.0266
O_2	1.36	0.0318
H_2O	5.46	0.0305
CCl_4	20.4	0.1383

EoS non-monotonic → liquid-gas instability.
High compression: real (vdW model) gases collapse (p decreases with decreasing V)
→ liquefaction

Correct EoS for unphysical instability:
Maxwell Construction

Steam Tables

Absolute pressure (kPa, kN/m^2)	Temperature (^oC)	Specific Volume (m^3/kg)	Density - ρ - (kg/m^3)	Specific Enthalpy of Liquid - h_l - (kJ/kg)	Specific Enthalpy of Evaporation - h_e - (kJ/kg)	Specific Enthalpy of Steam - h_s - (kJ/kg)	Specific Entropy of Steam - s - (kJ/kgK)
0.8	3.8	160	0.00626	15.8	2493	2509	9.058
2.0	17.5	67.0	0.0149	73.5	2460	2534	8.725
5.0	32.9	28.2	0.0354	137.8	2424	2562	8.396
10.0	45.8	14.7	0.0682	191.8	2393	2585	8.151
20.0	60.1	7.65	0.131	251.5	2358	2610	7.909
28	67.5	5.58	0.179	282.7	2340	2623	7.793
35	72.7	4.53	0.221	304.3	2327	2632	7.717
45	78.7	3.58	0.279	329.6	2312	2642	7.631
55	83.7	2.96	0.338	350.6	2299	2650	7.562
65	88.0	2.53	0.395	368.6	2288	2657	7.506
75	91.8	2.22	0.450	384.5	2279	2663	7.457
85	95.2	1.97	0.507	398.6	2270	2668	7.415
95	98.2	1.78	0.563	411.5	2262	2673	7.377
100	99.6	1.69	0.590	417.5	2258	2675	7.360
101.33[1)]	100	1.67	0.598	419.1	2257	2676	7.355
110	102.3	1.55	0.646	428.8	2251	2680	7.328
130	107.1	1.33	0.755	449.2	2238	2687	7.271
150	111.4	1.16	0.863	467.1	2226	2698	7.223
170	115.2	1.03	0.970	483.2	2216	2699	7.181
190	118.6	0.929	1.08	497.8	2206	2704	7.144
220	123.3	0.810	1.23	517.6	2193	2711	7.095
260	128.7	0.693	1.44	540.9	2177	2718	7.039
280	131.2	0.646	1.55	551.4	2170	2722	7.014
320	135.8	0.570	1.75	570.9	2157	2728	6.969

p = 1 bar= 101.33 kN/m²

Water 0⁰C → 100⁰C.
→ 419 kJ/kg

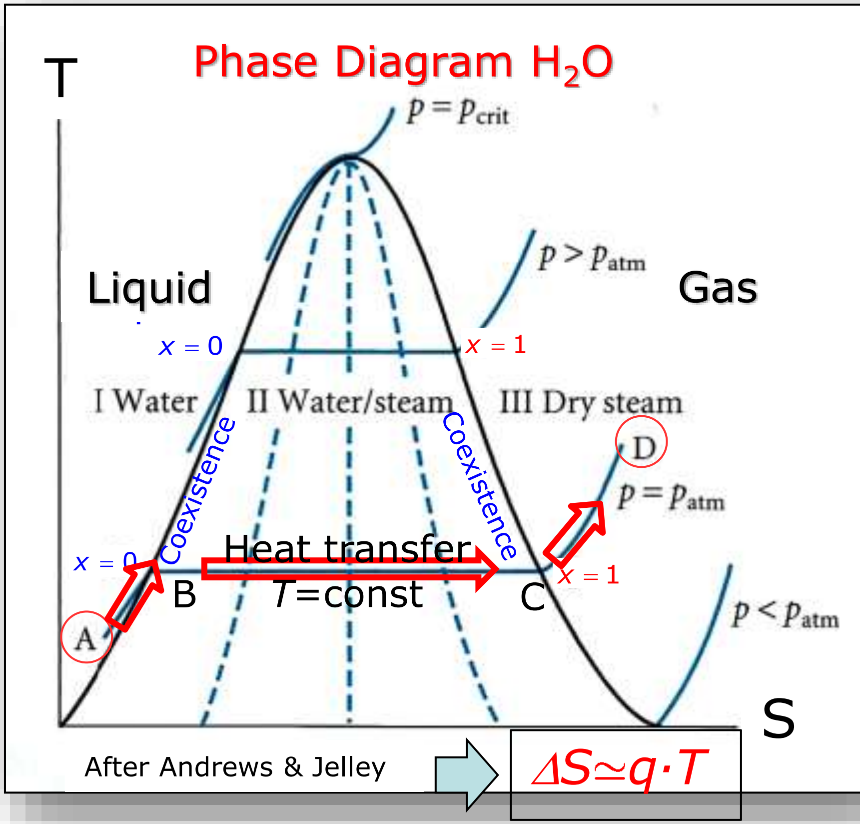
→ Specific enthalpy H_2O:
$h_{water}(100^0C) = 419\ kJ/kg$.

Specific enthalpy of evaporation (latent heat):
$h_{evap}(100^0C) = 2{,}257 kJ/kg$

$h_{steam}(100^0C) = 2.676 MJ/kg$

Latent Heat

Water as a Working Power Medium



To use steam as driving gas for thermal engines, heat energy has to be transferred to water at T_l (e.g., 25^{0}C)

A) heat 1mol liquid H_2O to 100^{0}C
B-C) evaporate all H_2O (@ 100^{0}C)
D) heat vapor beyond 100^{0}C→T_h

p = 1 atm *(bar)= 101.33 kN/m²*
→ Water boils @ at *100^{0}C*
→ Need *419 kJ/kg H_2O* to heat water from *0^{0}C* to *T= 100^{0}C*.

→ *@ p=101.33 kN/m²* and *100^{0}C*
Specific enthalpy H_2O:
$h_{water}(100^0C) = 419$ kJ/kg.

Specific enthalpy of evaporation (latent heat): $h_{evap}(100^0C) = 2{,}257$ kJ/kg
(not applicable to ideal gas)

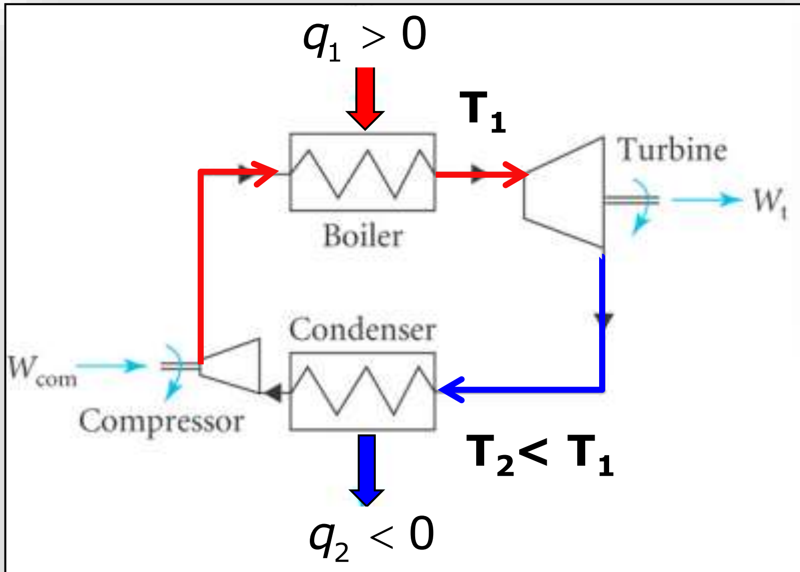
Total heat required at *p=const.* to convert H_2O to steam @*100^{0}C* :

$h_{steam}(100^0C) = (419 + 2{,}257)$kJ/kg = 2,676 kJ/kg = 2.676 (MJ/kg) = 0.74 kWh/kg

L-G mixture	$h_s(x) = (1-x)\cdot h_{water} + x\cdot h_{steam}$
Similar:	$u_s(x) = (1-x)\cdot u_{water} + x\cdot u_{steam}$

Extensive variables
(U, H, S,..)

S-T Diagram for Steam Carnot Process



T(K)	p (bar)	h (kJ kg^{-1}) h_{fl}	h_{gas}	s (kJ kg^{-1} K^{-1}) s_{fl}	s_{gas}
303	0.04	126	2556	0.436	8.452
625	170	1690	2548	3.808	5.181

Enthalpy, entropy extensive→ Scale w/ x

$$x = \textit{steam quality}\ (\textit{fraction}\ g/(g+fl))$$

$$h = (1-x)\cdot h_{fl} + x\cdot h_{gas} \qquad h = H/\textit{unit mass}$$

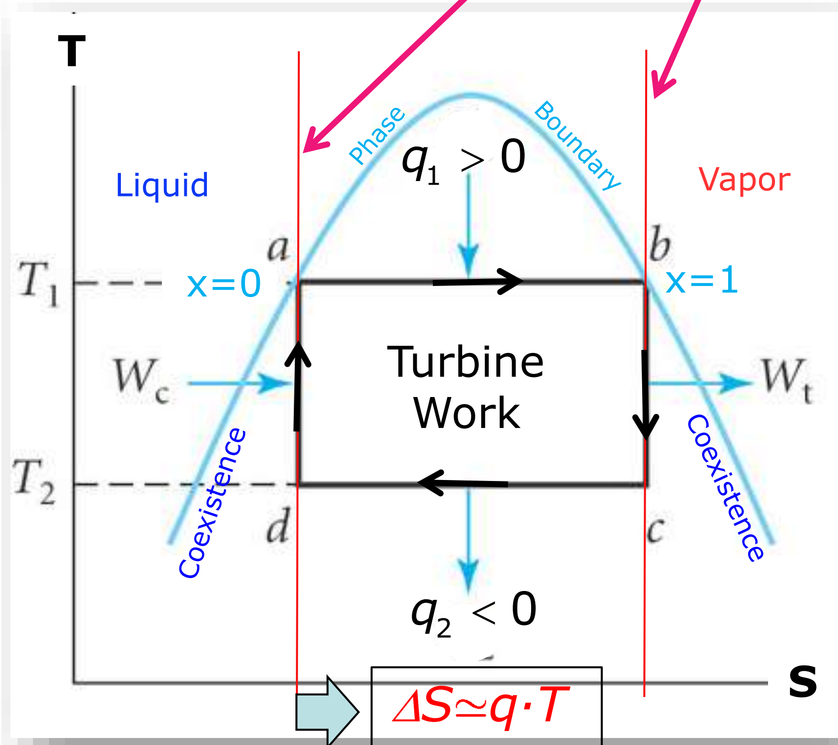
$$s = (1-x)\cdot s_{fl} + x\cdot s_{gas} \qquad s = S/\textit{unit mass}$$

$$\textit{Example}: s(d) = s(a) = 3.808\frac{kJ}{kg\cdot K}$$

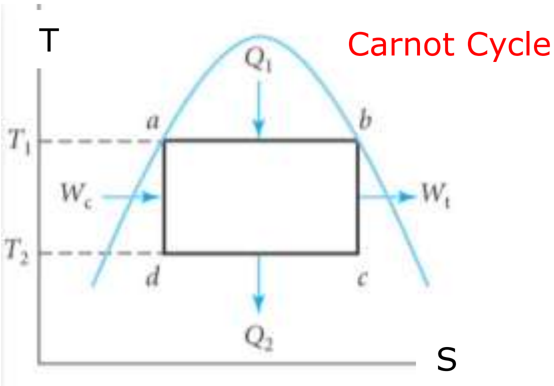
$$s(d) = (1-x_d)\cdot \underset{0.436}{s_{fl}} + x_d\cdot \underset{8.452}{s_{gas}} = 3.808$$

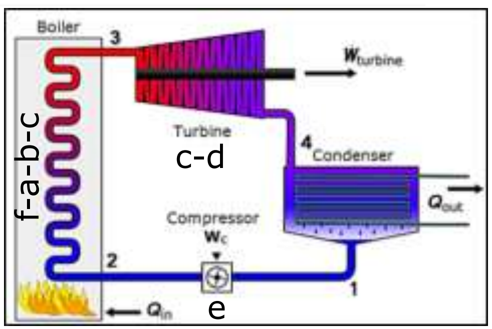
$$\rightarrow \textit{Solve for}\ x_d = 0.42,\ \ ....$$

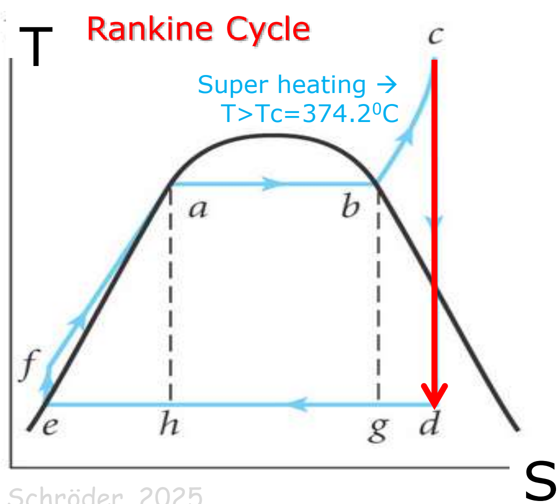
After Andrews & Jelley



Rankine Steam Cycle







Carnot cycle: highest possible work output per q for T=const. processes.
Works well for ideal gases (simple molecules, high T)

Disadvantage for real gases and moderate T, because phase coexistence region limits gas $\boldsymbol{T_h}$ per $\boldsymbol{q}_{in}$
q= T·ΔS in Carnot process, i.e., T_h is limited → low ε

Rankine cycle: (Thermodynamically robust)

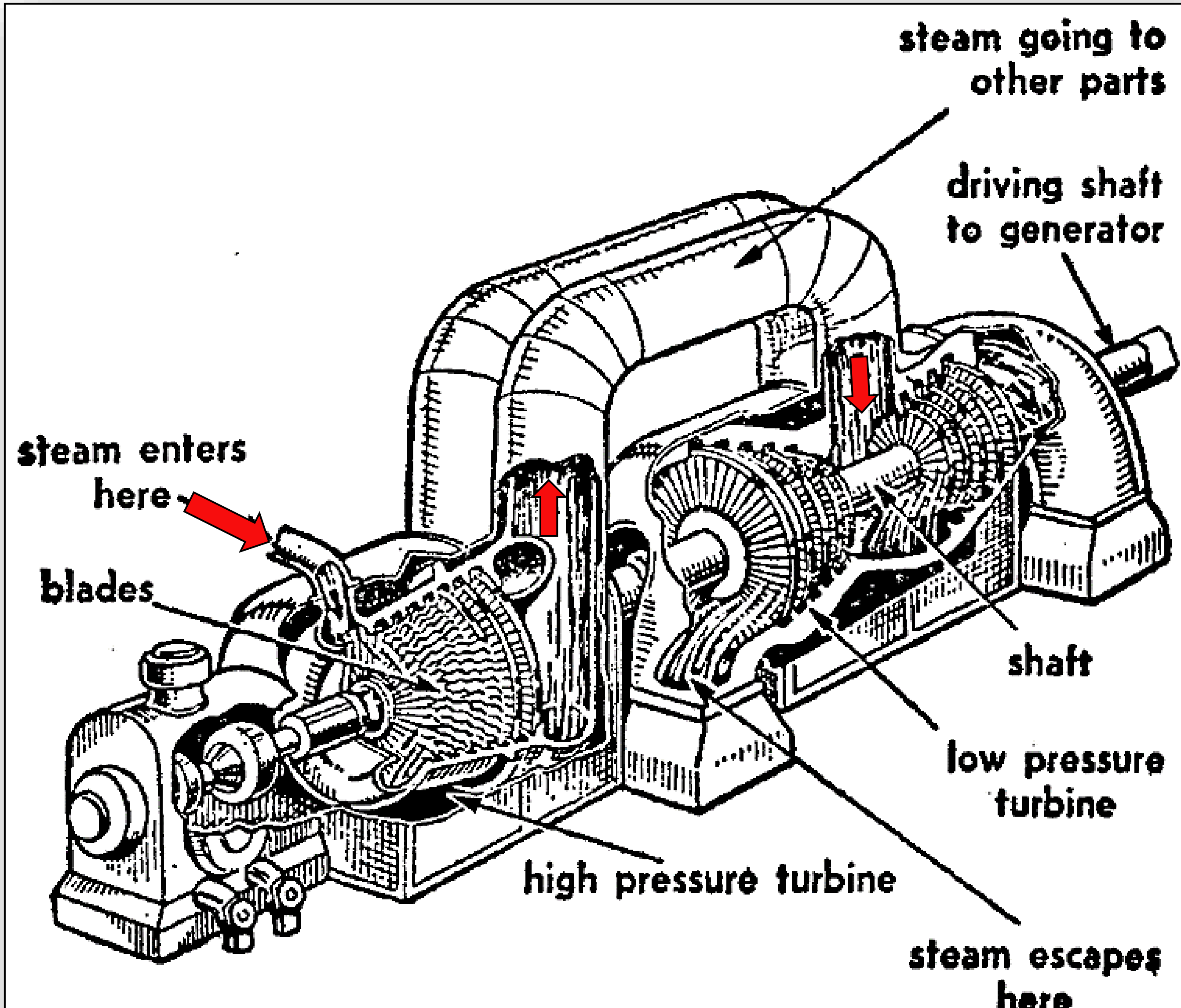
e → *f* Compressor (pump) injects H_2O under *p*
f → *a* Economizer heats H_2O under pressure.
a → *b* Evaporator boils H_2O under p = const.
b → *c* Superheater heats steam @high p = const.
c → *d* Turbine produces work, expands steam

$$w_{Turbine} = H_c - H_d = \Delta\left(U + p \cdot V\right) = \int_c^d V \cdot dp \quad (S = const.)$$

d → *e* condenser liquifies vapor @ $p < p_{at}$.
Heating and cooling occur at p=const.

Efficiency: $\varepsilon_{Rankine} = \dfrac{w_{Turbine} - w_{Compressor}}{Q_{in}} = 0.3 - 0.5$

Low/Medium Pressure Steam Turbines



Agenda: Thermal Power Plants

- Operational principle of cyclic thermodynamic engines
  - Entropy, heat, and work in Carnot cycle
- Reciprocating (piston) engines
  - Steam cylinder
  - Stirling engine
  - Otto internal combustion cycle
- Steam power plants
  - Isotherms of real gases
  - Steam and air as working media
  - S-T cycles for Carnot, Rankine, and Brayton cycles
- Gas turbine power plants
  - Gas turbine operation, enthalpy balance
  - Combined-cycle plants
- Chemistry of complete & incomplete combustion
  - Examples
- Carbon (CO_2) capture processes

Next: Power from nuclear transmutation
Andrew & Jelley Chs. 9 & 10