ChemE 2200 – Chemical Thermodynamics Lecture 6

Today:

Heat Engines and Heat Pumps.
The Carnot Cycle.
The Rankine, Otto, and Diesel Cycles.

Defining Question:

“What is a Carnot Cycle?”

Reading for Today’s Lecture:

McQuarrie & Simon, Chapter 20.7.

Reading for Thermodynamics Lecture 7:

McQuarrie & Simon, Chapter 21.1-21.5

1st Prelim

Tuesday, March 11, 7:30 – 9:30 p.m.

245 Olin Hall

Covers –
- Atomic Orbitals
- Molecular Orbitals
- Atomic and Molecular Spectroscopy
- Electrons in Solids
- Classical Thermodynamics through 1st Law

Covers –
- Lectures through 1st half of Monday, 2/24 (Lecture T4)
- Homework through Homework 5
- Calculation Sessions through Calculation Session 5

You may use a hand-written, double-sided reference sheet.
Reference sheets will be submitted with the Prelim.
Reference sheets will be returned Wednesday, March 12.

Team Competition Wednesday March 12: “How well Do you know Your peers?”

ChemE 2200 – Physical Chemistry II for Engineers
Calculation Session 8 – March 13, 2024 – Team Competition

Team Name: ______________________

How well do you know the ChemE Class of 2026?

Use each of the following names exactly once to match the student names with their unique traits.

Julia Arnold	**Emily Destito**	**Vivian Liu**	**Anthony Parlatore**	**Hayden Spector**
Quinn Baker	**Ronin Ford**	**Johhny Lowry**	**Sofia Patterson-Melendrez**	**Rakshith Sreeram**
Adam Belew	**Jessica Gart**	**William Manno**	**Jake Pena**	**Kayla Stephenson**
Clare Belman	**Kristina Georges**	**Xander Marroquin**	**Sofia Salazar**	**Rafael Tassari**
Lara Capellino	**Liam Gillespie**	**Sean McInnis**	**Veranika Sasina**	**Avantika Vaish**
Sam Chang	**Ryan Hamel**	**Chimdinma Muoguilim**	**Neil Shah**	**Timothy Walsh**
James Chen	**Chike Iwuala**	**Dipo Omakanwaye**	**Athavan Shanmuganathan**	**Amy Wu**
Kong Chen	**Angel Liang**	**Madeline Ortiz**	**Stephen Smith**	**Ari Zucker**

Name	Trait
Amy Wu	I was the best in the world in Percy Jackson trivia on QuizUp.
James Chen	I have moved around five times in my life.
Jake Pena	I have dual citizenship (US and Canada).
Clare Belman	I started skiing when I was 2 years old.
Xander Marroquin	I am very scared of bats.
Anthony Parlatore	I lived in Saudi Arabia for 13 years.
Sean McInnis	I have never drank coffee.
Sofia Salazar	I drove into my garage.
Hayden Spector	I flooded the chemistry classroom on the first day of high school.
Dipo Omokanwaye	I fought an Olympic-level athlete.
Chike Iwuala	I lived in Nigeria until I was 12.
Rafael Tassari	I can keep cracking my knuckles indefinitely.
Kayla Stephenson	I have never had a poke bowl.
Neil Shah	I can juggle a soccer ball more than 100 times (with warmup).
Avantika Vaish	I went paragliding in Switzerland.
Johnny Lowry	I salsa, but I do not guacamole (or break dance ☹).
Liam Gillespie	I was born in Alabama and have lived in 5 states.
Ryan Hamel	I am a member of the Cornell Bowling Club.
Julia Arnold	I danced ballet when I was younger.
Ronin Ford	I drink [7, 10) glasses of milk daily.

Name	Trait
Vivian Liu	I do a fantastic worm.
Ari Zucker	I had the cops called on me for building a wooden fort in the woods.
Kong Chen	I almost went deaf in my left ear.
Veranika Sasina	I dance more than 20 hours per week.
William Manno	I have perfect pitch.
Stephen Smith	I backpacked over 200 miles of the Appalachian Trail.
Athavan Shanmuganathan	I accidentally slept through a meeting with my celebrity cousin.
Rakshith Sreeram	My leg has been run over by a car.
Timothy Walsh	I was the leader of a Pottery Club in high school.
Emily Destito	I can ride a unicycle.
Lara Capellino	I gave a one-minute speech at the U.S. Capitol.
Quinn Baker	My favorite book series is Dune.
Angel Liang	I have the same first name as a CS professor at Cornell.
Chimdinma Muoguilim	I haven't celebrated my birthday with family since I was 11 because of boarding school.
Madeline Ortiz	I almost exclusively ate pasta with cheese for lunch through all of high school.
Jessica Gart	I am bilingual and did not learn English until I was 4.
Sofia Patterson-Melendrez	My dad was my high school principal.
Kristina Georges	I owned 23 chickens at once.
Sam Chang	I was varsity riflery captain in high school.
Adam Belew	I own two kayaks.

Recap

1st Law of Thermodynamics: $dU = \delta q + \delta w$

2nd Law of Thermodynamics: $\Delta S > 0$ for spontaneous processes.

$$\Delta S = \int \frac{\delta q_{\text{rev}}}{T}$$

$$\delta q_{\text{rev}} = dU - \delta w_{\text{rev}}$$

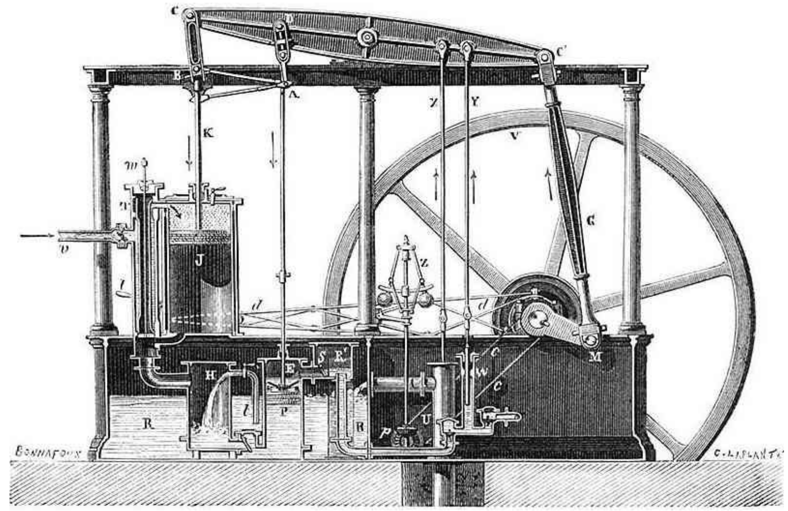
Combining the 1st and 2nd Laws of Thermodynamics:

$$TdS = dU + PdV$$

Heat Engines

heat → work

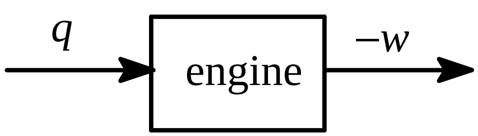
thermo dynamics



Thermodynamics was developed to analyze and improve steam engines in the early 1800s.

"Steam engines contributed more to thermodynamics than thermodynamics contributed to steam engines."

Nicolas Léonard Sadi Carnot (1796 – 1832) French Mechanical Engineer

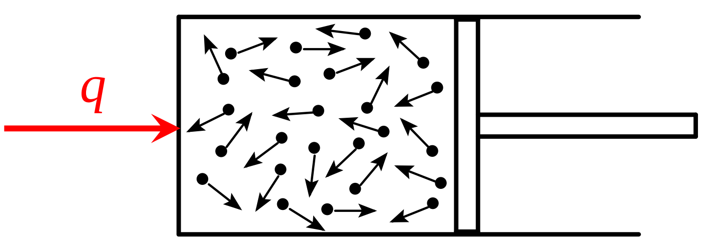


How much heat can be converted to work?

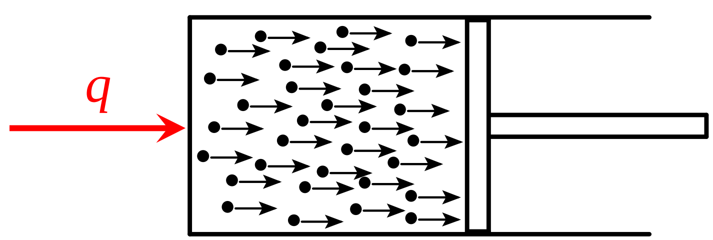
How to improve efficiency?

1st Law analysis: $-w = q$ 100% efficiency possible?

2nd Law analysis: Consider a molecular basis



heat increases internal energy, more molecular K.E.



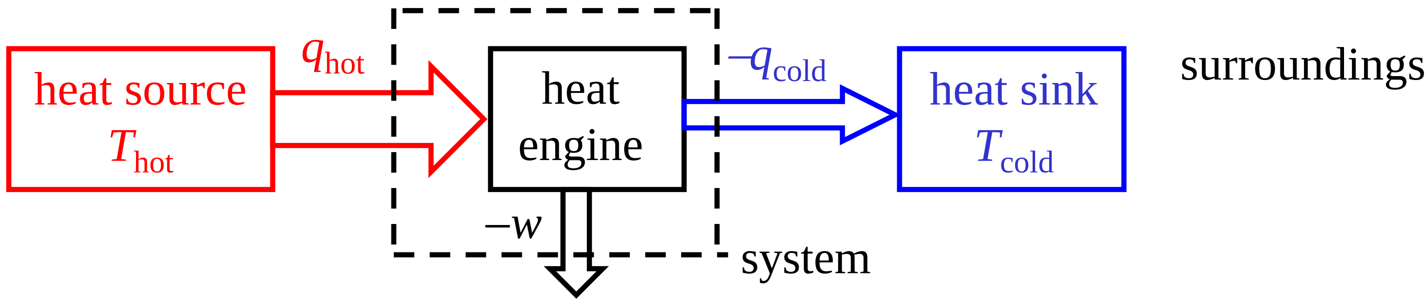
to convert *all* heat to work on the piston, all molecular motion must be toward piston.

Improbable. Efficiency is limited by the 2nd law.

Heat Engines

Thermal energy is converted to mechanical energy.

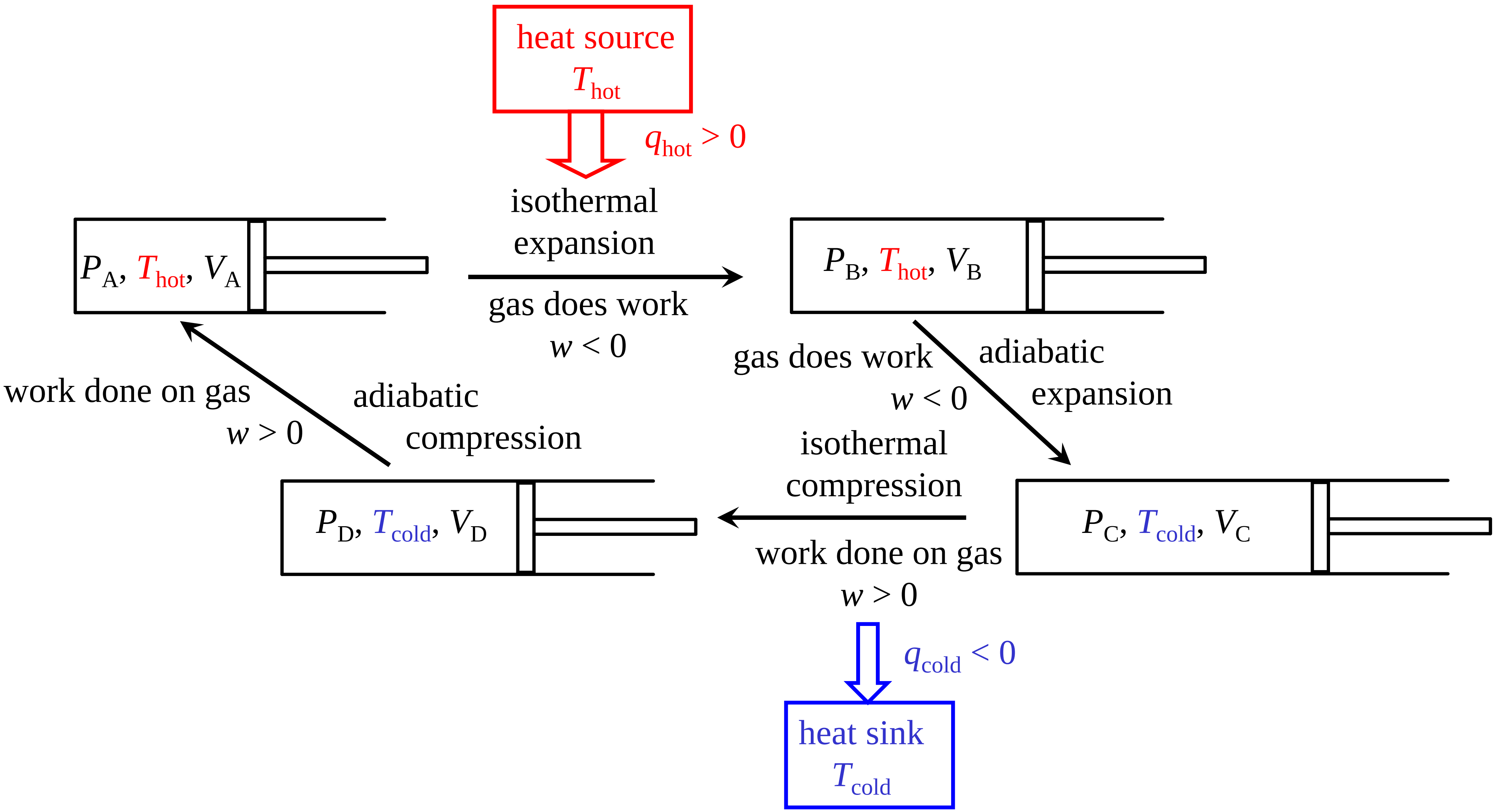
2nd Law: cannot convert all heat to work; some heat must be discarded.



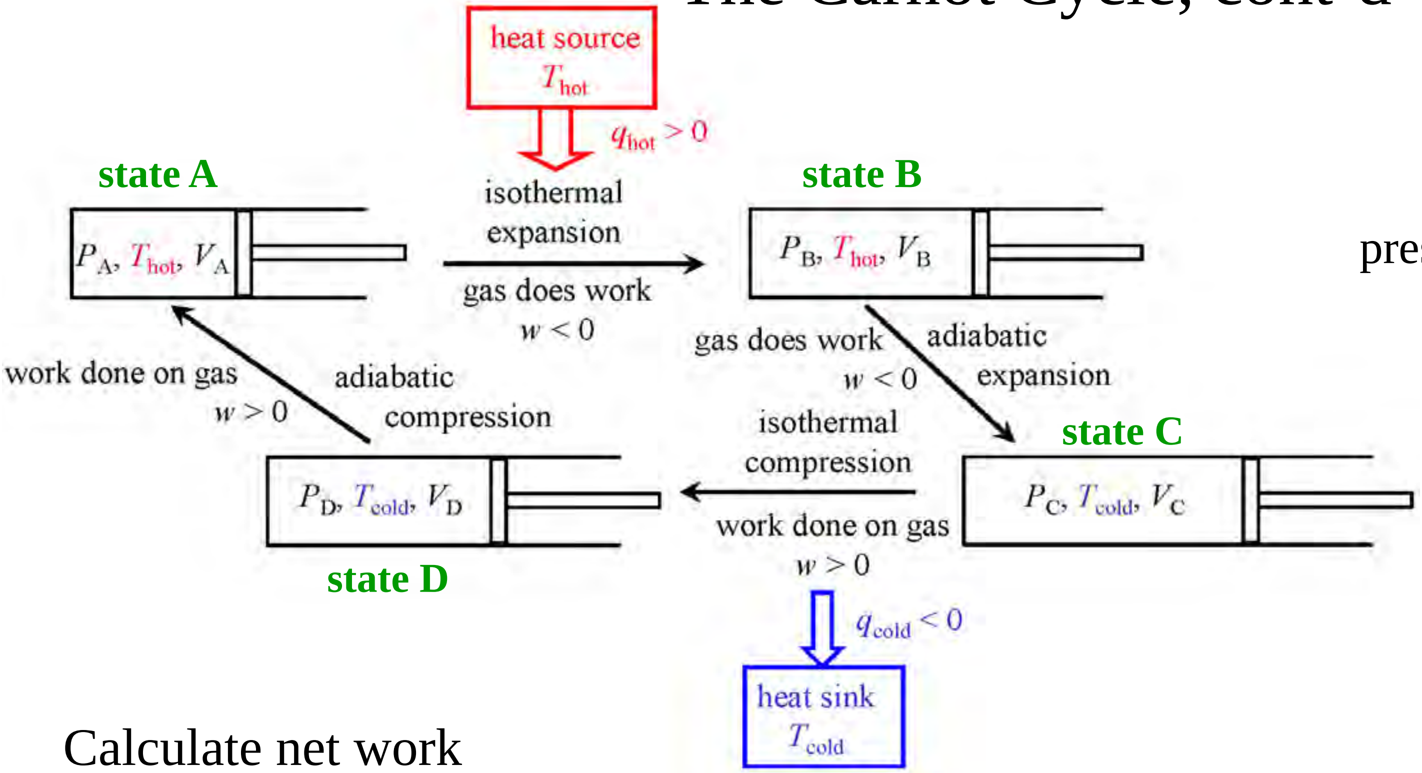
The Carnot Cycle for a Heat Engine

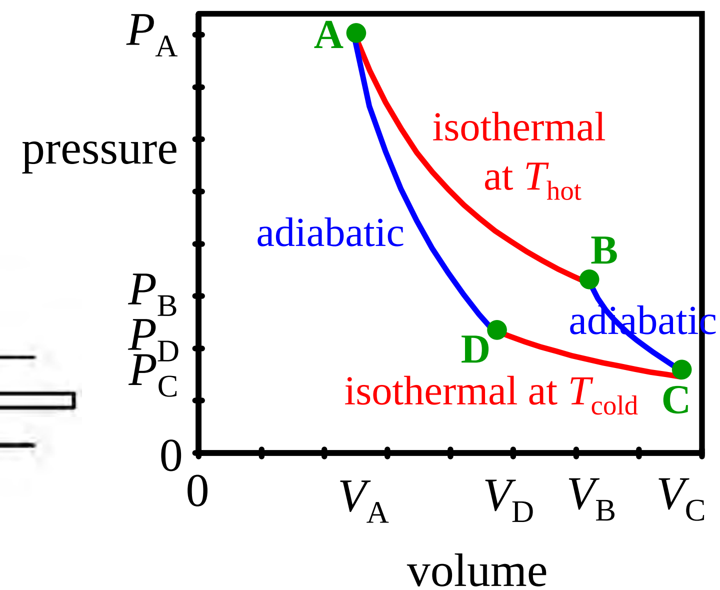
Thermal energy is converted to mechanical energy.

Working fluid is an ideal gas.



The Carnot Cycle, cont'd





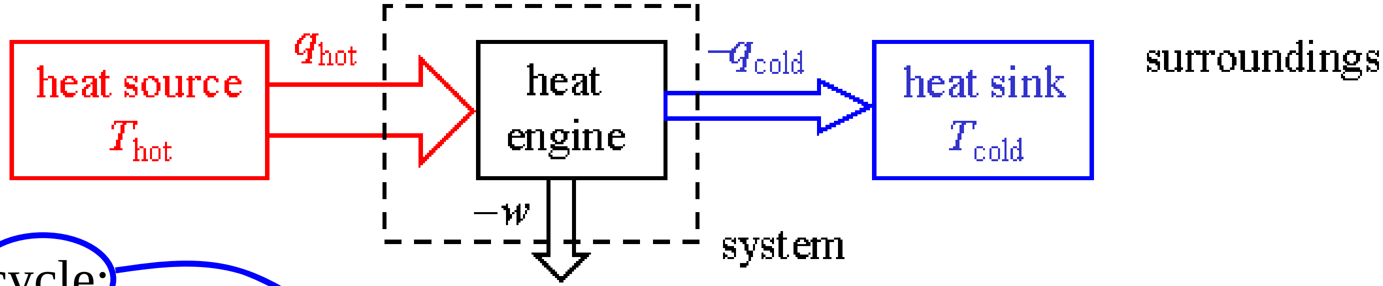
Calculate net work

$$w = -\int_A^B PdV - \int_B^C PdV + \int_C^D PdV + \int_D^A PdV$$

$$= \underbrace{\left[-\int_A^B PdV - \int_B^C PdV \right]}_{\text{area under A-B-C}} - \underbrace{\left[-\int_C^D PdV - \int_D^A PdV \right]}_{\text{area under A-D-C}}$$

net work = area enclosed by cycle

The Carnot Cycle, cont'd



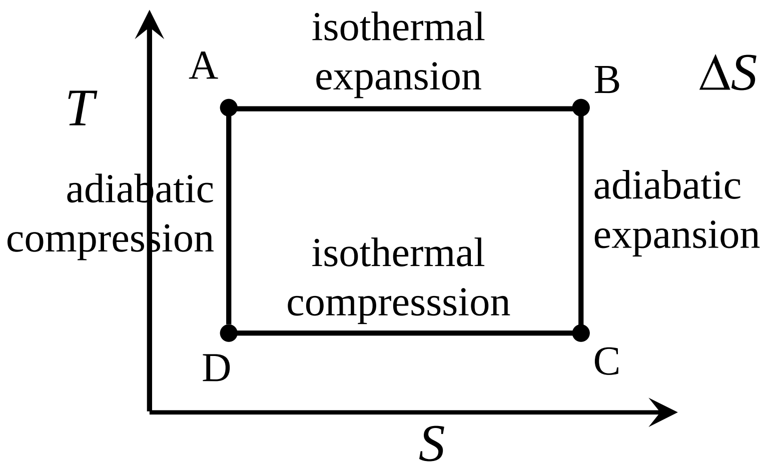
1^{st} Law analysis of cycle:

$$\Delta U_{engine} = 0 = w_{cycle} + q_{rev,hot} + q_{rev,cold}$$

$$\text{maximum efficiency} = \frac{-w}{q_{rev,hot}} = \frac{q_{rev,hot} + q_{rev,cold}}{q_{rev,hot}} < 1$$

substitute

2^{nd} Law analysis of cycle: Plot on a map of S and S's complementary parameter, T



$$\Delta S = 0 = \int_A^B dS + \int_C^D dS = \int \frac{\delta q_{rev,hot}}{T_{hot}} + \int \frac{\delta q_{rev,cold}}{T_{cold}}$$

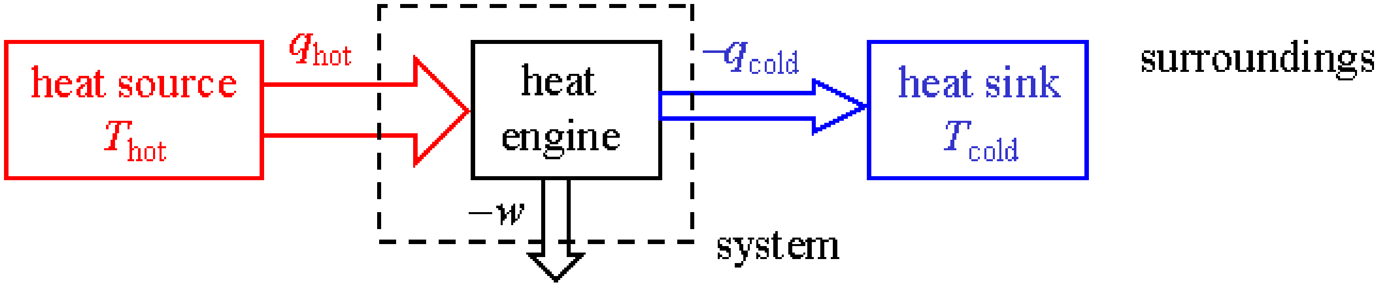
$$q_{rev,cold} = -q_{rev,hot}\left(\frac{T_{cold}}{T_{hot}}\right)$$

Actual engines do not have reversible paths.

$$\text{maximum efficiency} = \frac{q_{rev,hot} - q_{rev,hot}\left(\frac{T_{cold}}{T_{hot}}\right)}{q_{rev,hot}} = \frac{T_{hot} - T_{cold}}{T_{hot}}$$

Actual engines have lower efficiencies.

The Carnot Cycle Efficiency



$$\text{Carnot cycle efficiency} = \frac{\text{work from engine}}{\text{heat from hot source}} = \frac{T_{hot} - T_{cold}}{T_{hot}}$$

For steam at 1 atm, T_{hot} = 100°C (373K) and ambient cooling T_{cold} = 25°C (298K)

$$\text{Carnot cycle efficiency} = \frac{T_{hot} - T_{cold}}{T_{hot}} = \frac{373 - 298}{373} = 0.20$$

For atomic energy typical T_{hot} = 950°C (1220K) and typical cooling T_{cold} = 450°C (720K)

$$\text{Carnot cycle efficiency} = \frac{T_{hot} - T_{cold}}{T_{hot}} = \frac{1220 - 720}{1220} = 0.41$$

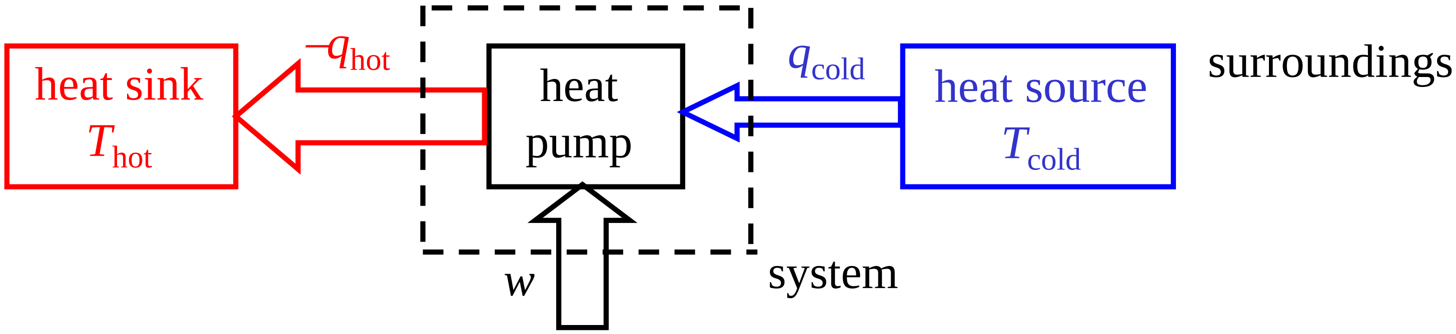
For T_{cold} = 0K, efficiency = 1.

For $T_{hot} = T_{cold}$, efficiency = 0.

Heat Pumps

Thermal energy is pumped from a cold source to a hot sink.

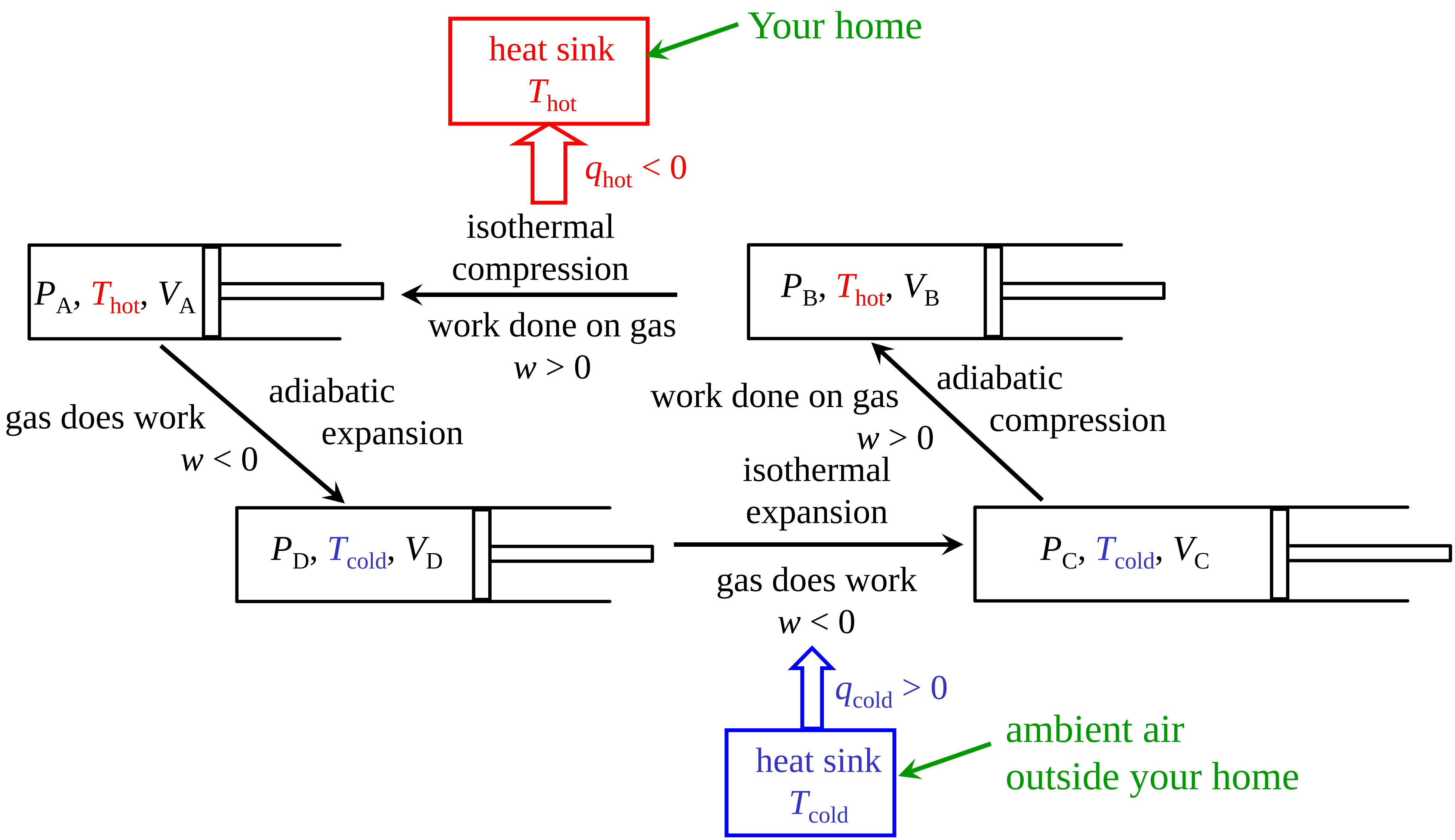
2^{nd} Law: Heat does not spontaneously flow from cold to hot. Must provide work.



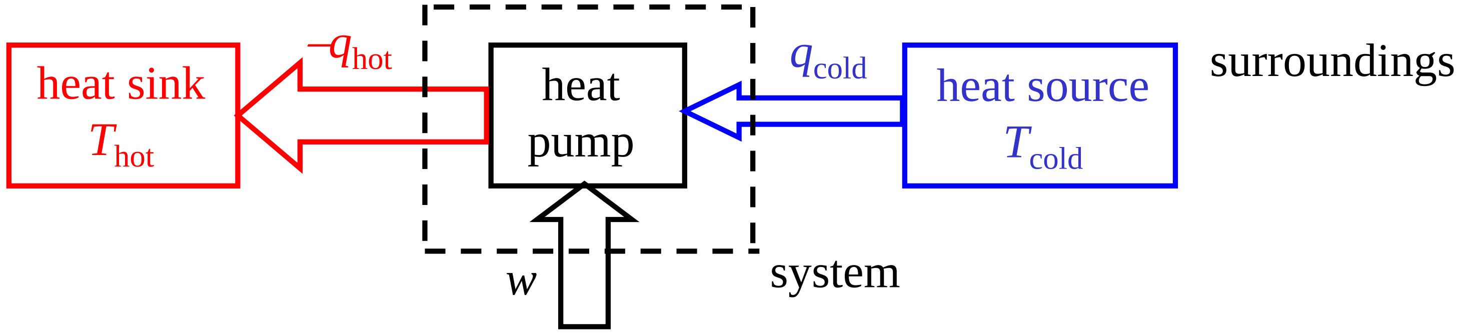
The Carnot Cycle for a Heat Pump

The Carnot Cycle: Four States Connected by Four Reversible Paths.

Working fluid is an ideal gas.



The Carnot Cycle Efficiency



$$\text{Carnot cycle efficiency} = \frac{\text{work to heat pump}}{\text{heat to hot sink}} = \frac{T_{hot} - T_{cold}}{T_{hot}}$$

For a home at T_{hot} = 20°C (293K) and outside air at T_{cold} = 0°C (273K)

$$\text{work to heat pump} = \left(\frac{T_{hot} - T_{cold}}{T_{hot}}\right)(\text{heat to hot sink})$$

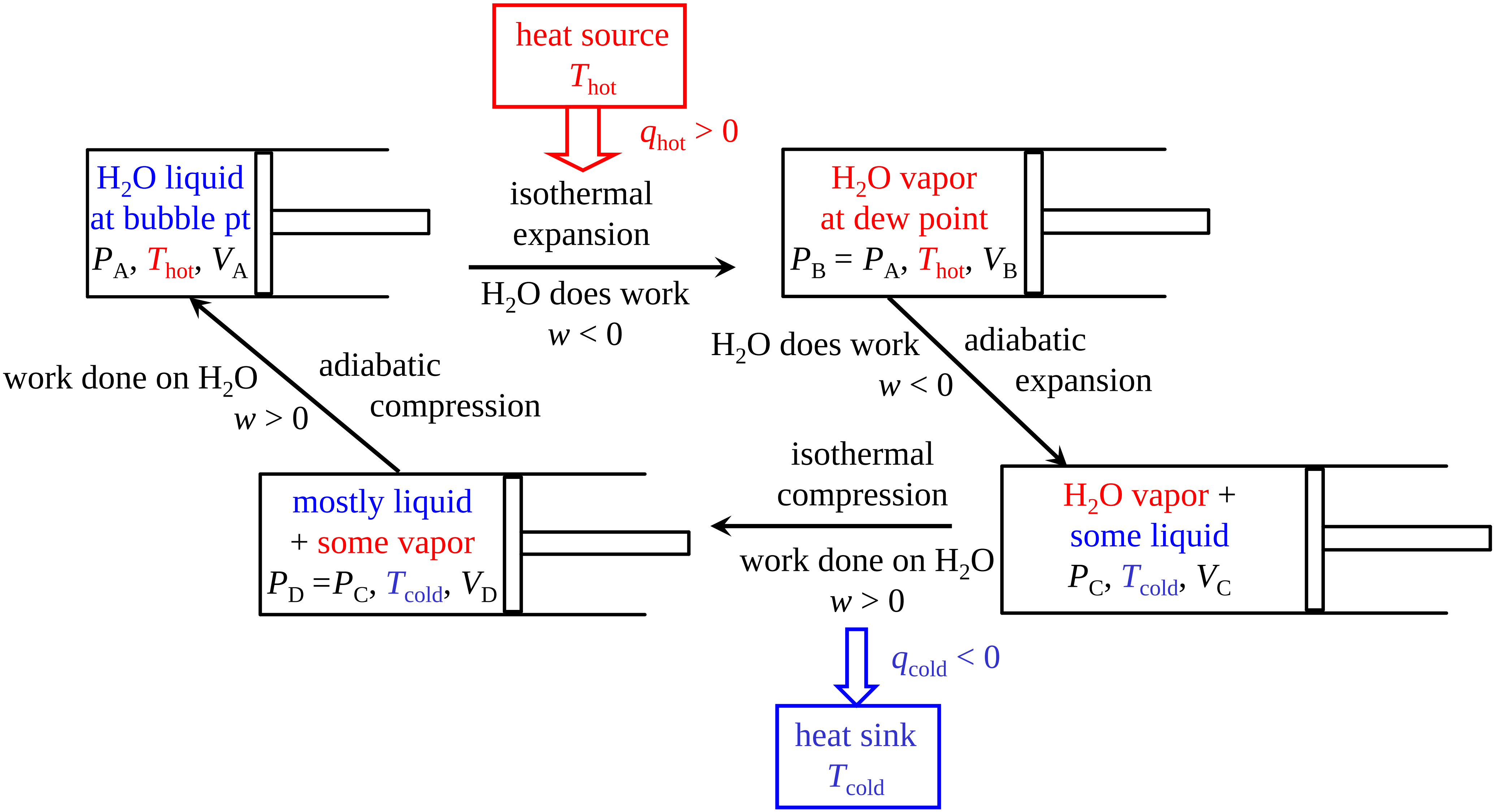
$$= \left(\frac{293 - 273}{293}\right)(\text{heat to hot sink})$$

$$= 0.07(\text{heat to hot sink})$$

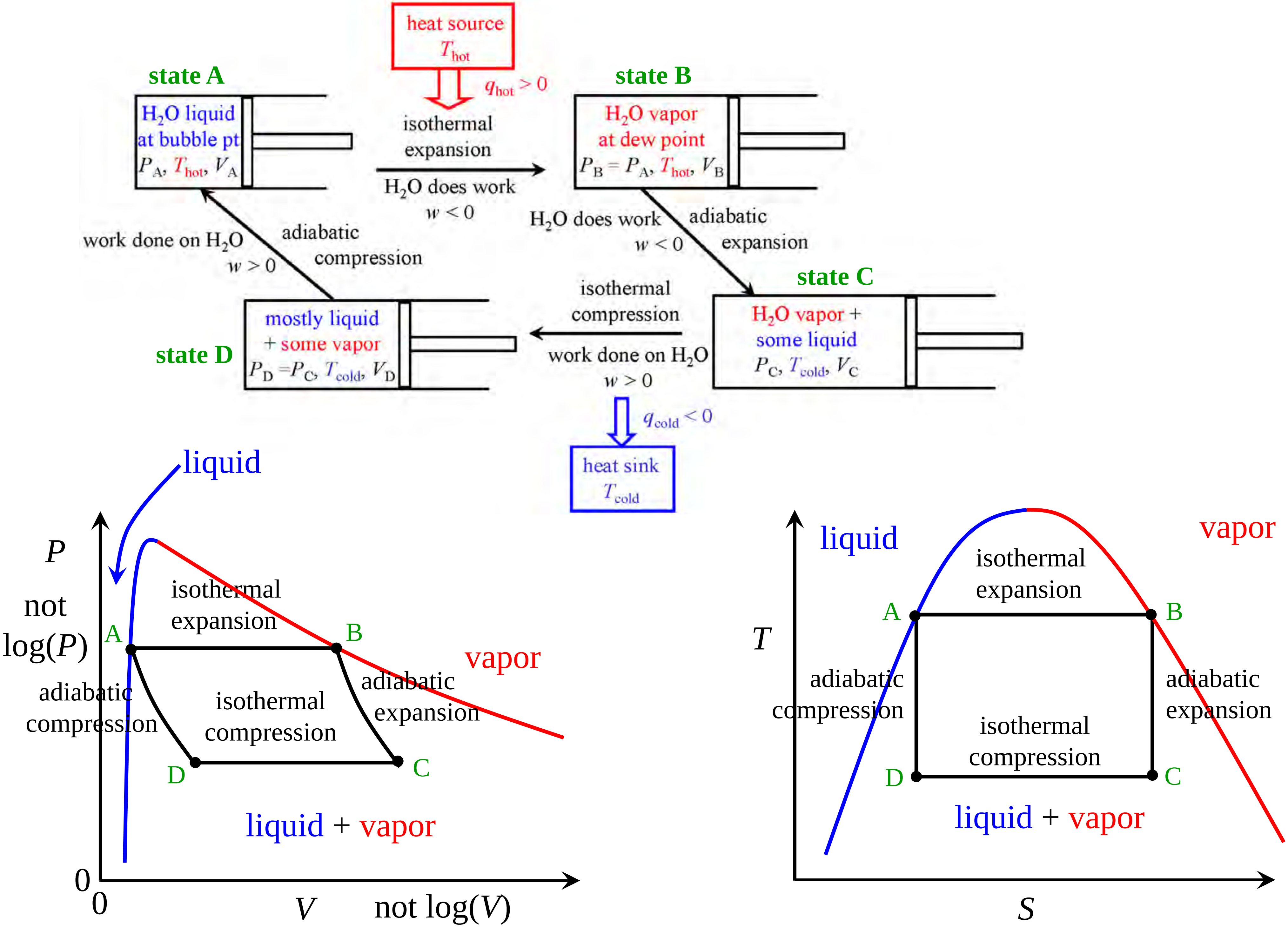
An electric heater would require 1000 kW, whereas a heat pump requires only 70 kW.

The Carnot Water-Steam Cycle for a Heat Engine

Working fluid is H_2O - liquid and vapor

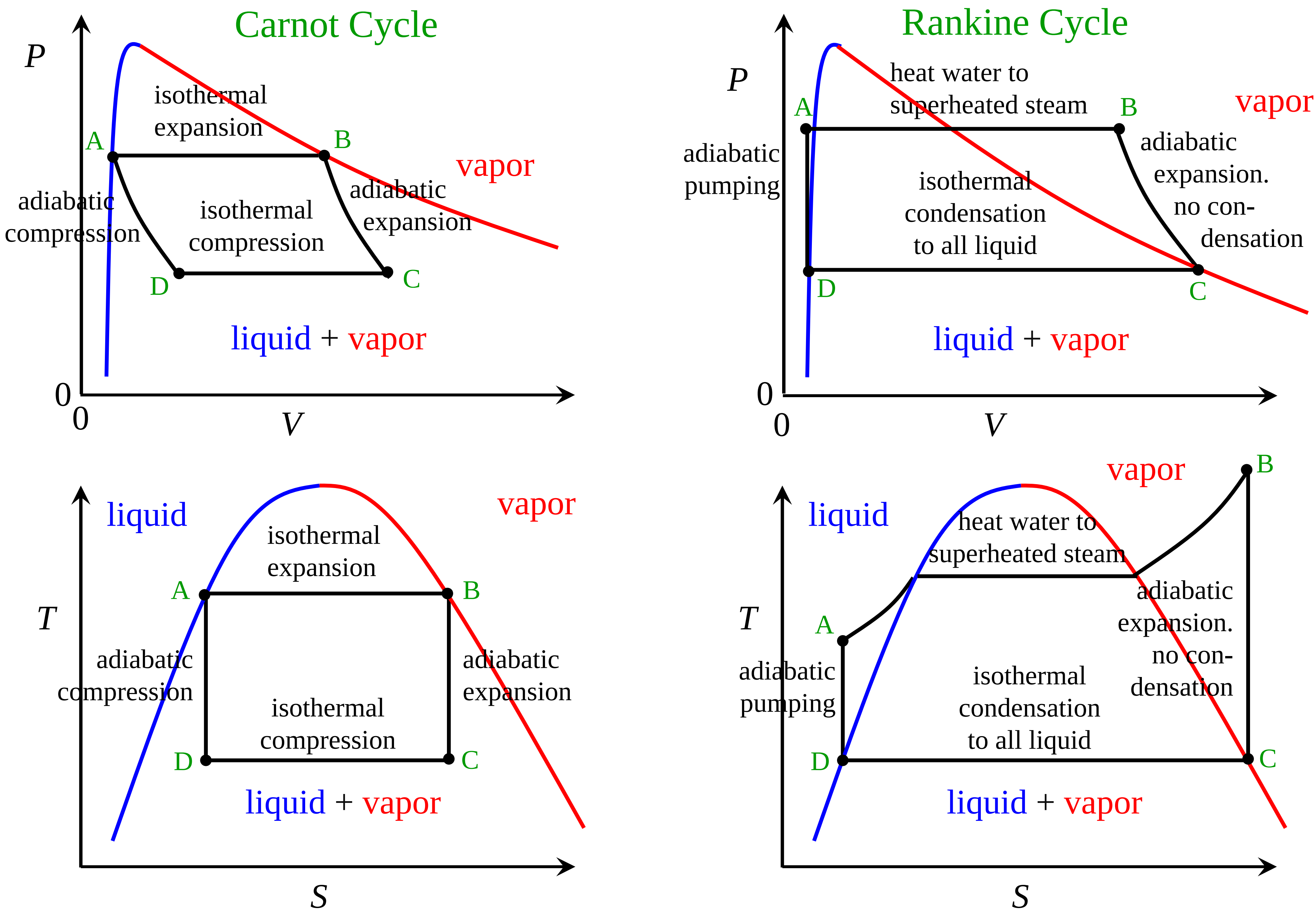


The Carnot Water-Steam Cycle for a Heat Engine



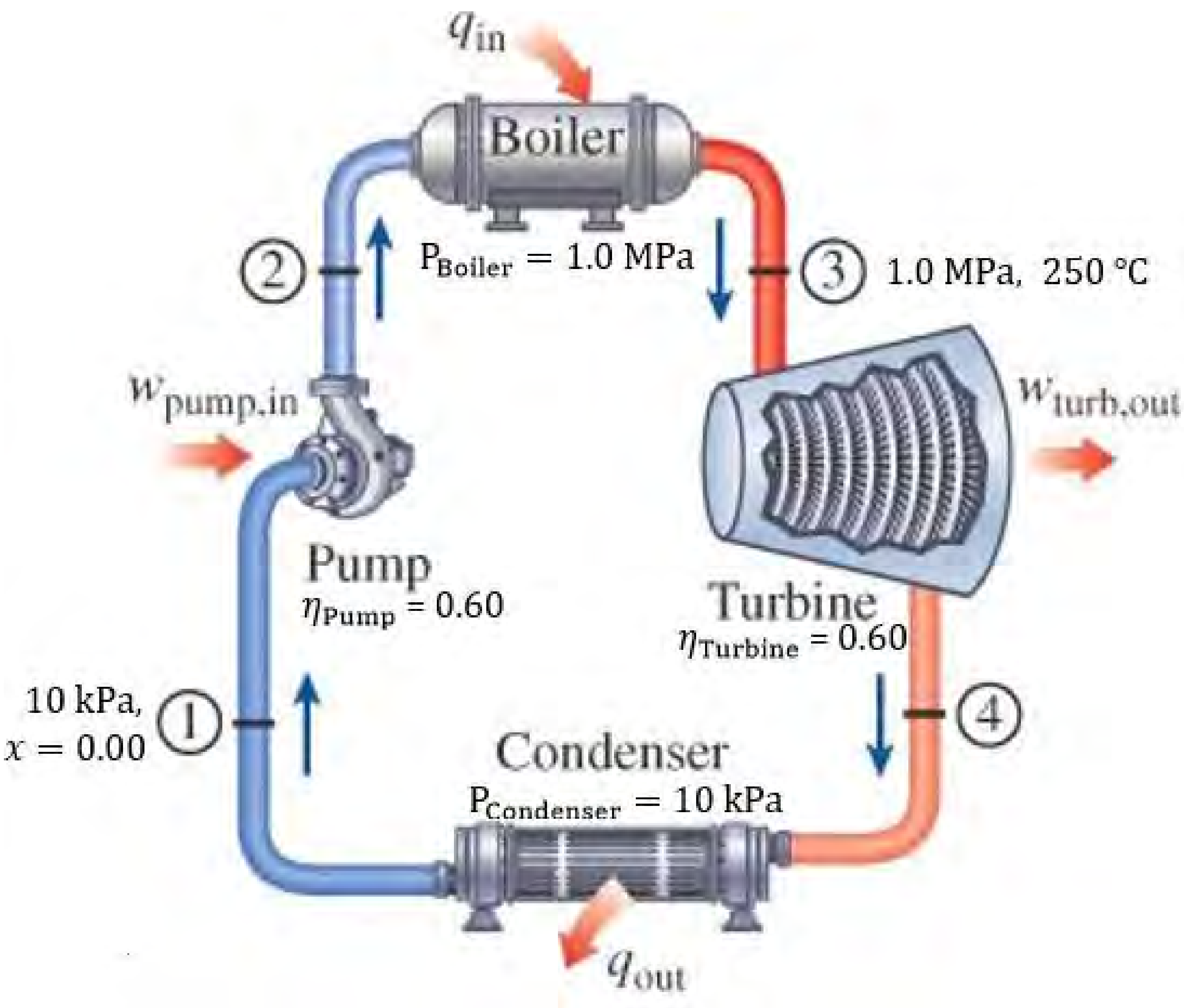
The Rankine Water-Steam Cycle for a Heat Engine

Similar to Carnot Cycle, but expand 100% vapor and compress 100% liquid.



The Rankine Water-Steam Cycle for a Heat Engine

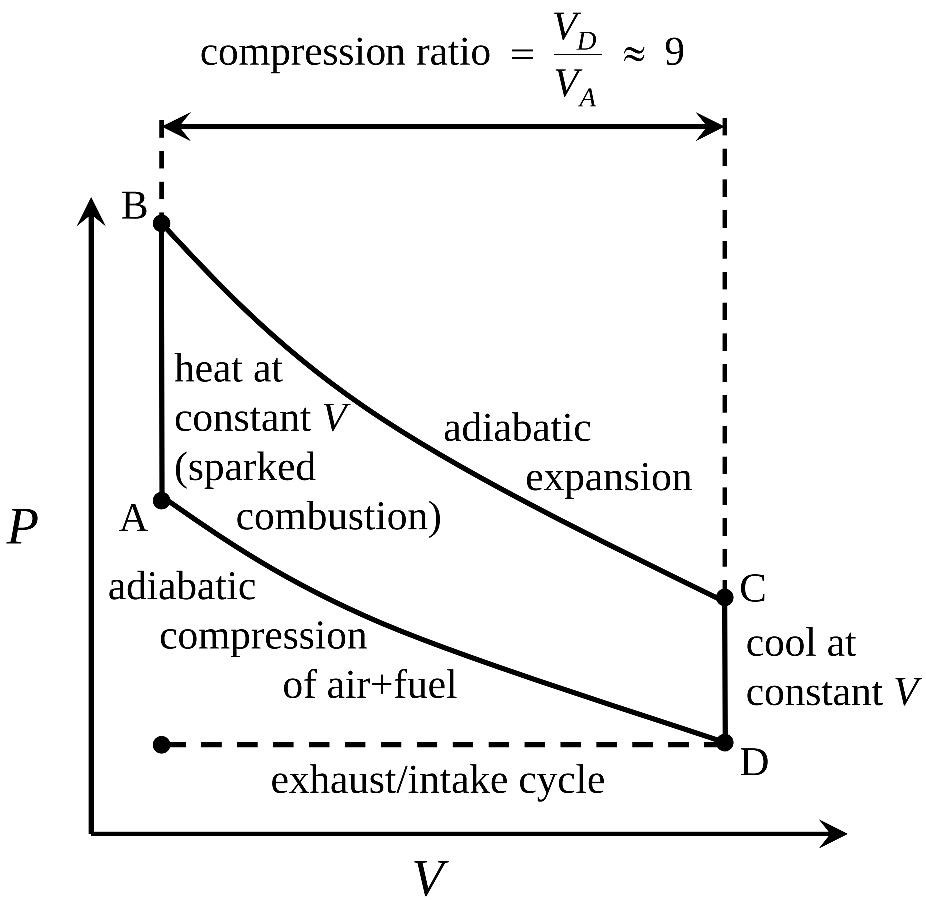
Similar to Carnot Cycle, but expand 100% vapor and compress 100% liquid.

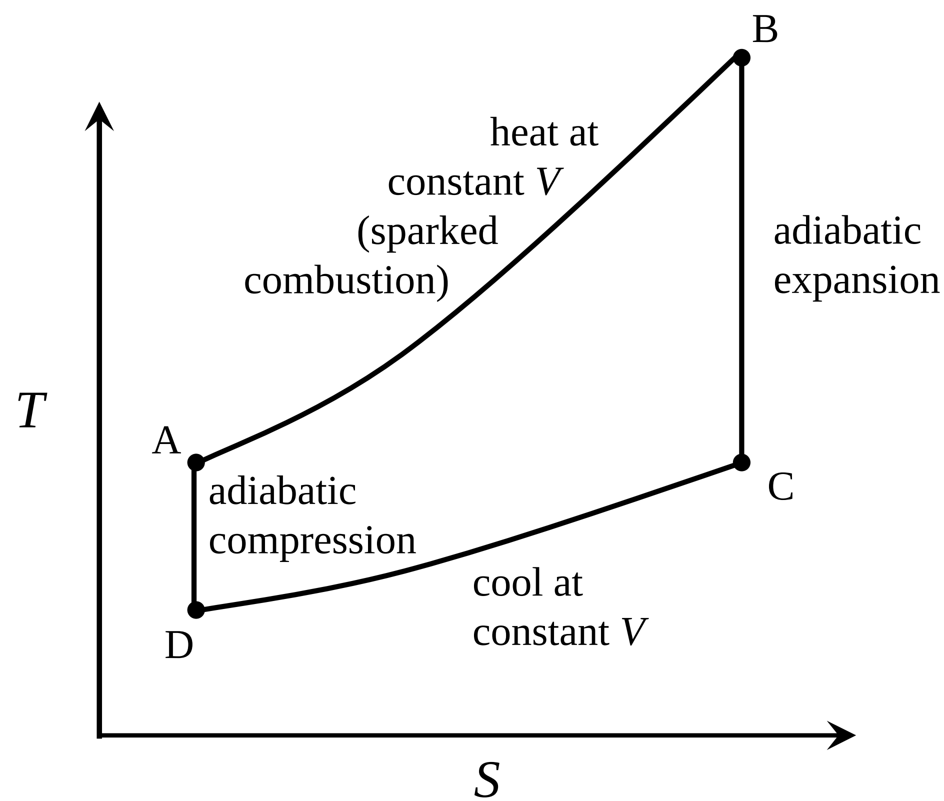


William Rankine
1820-1872

The Otto Cycle for a Heat Engine

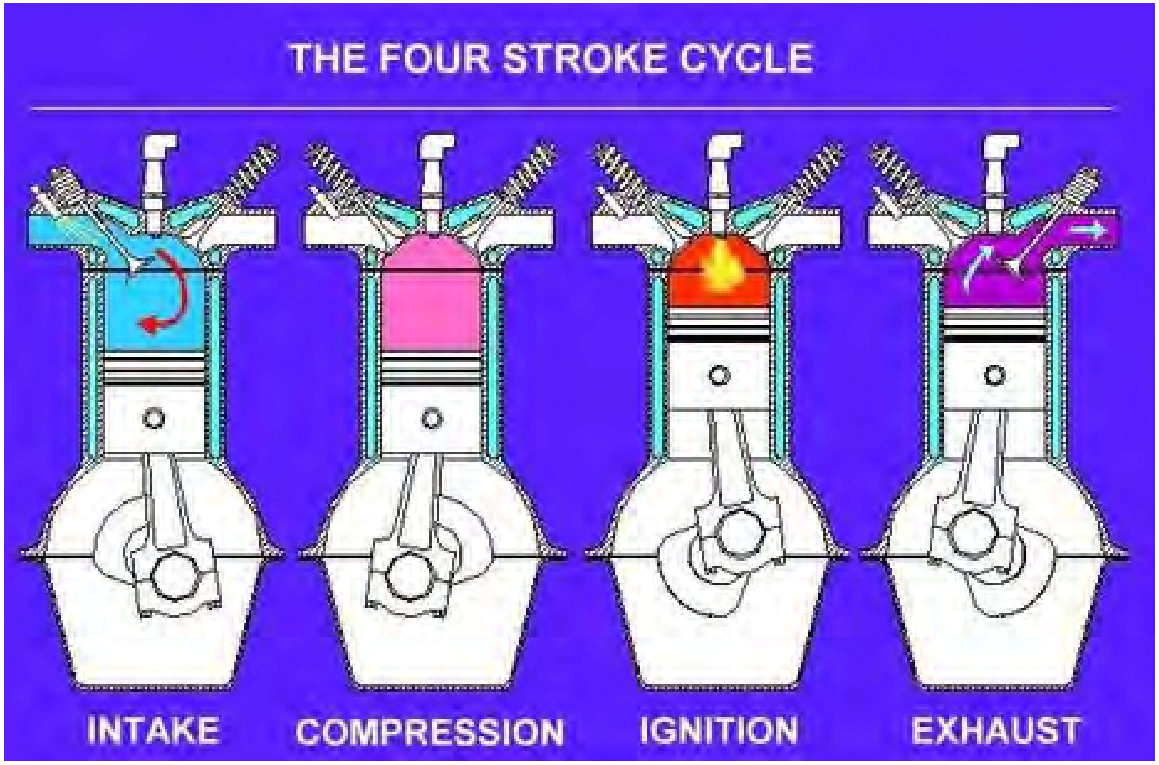
An internal combustion engine



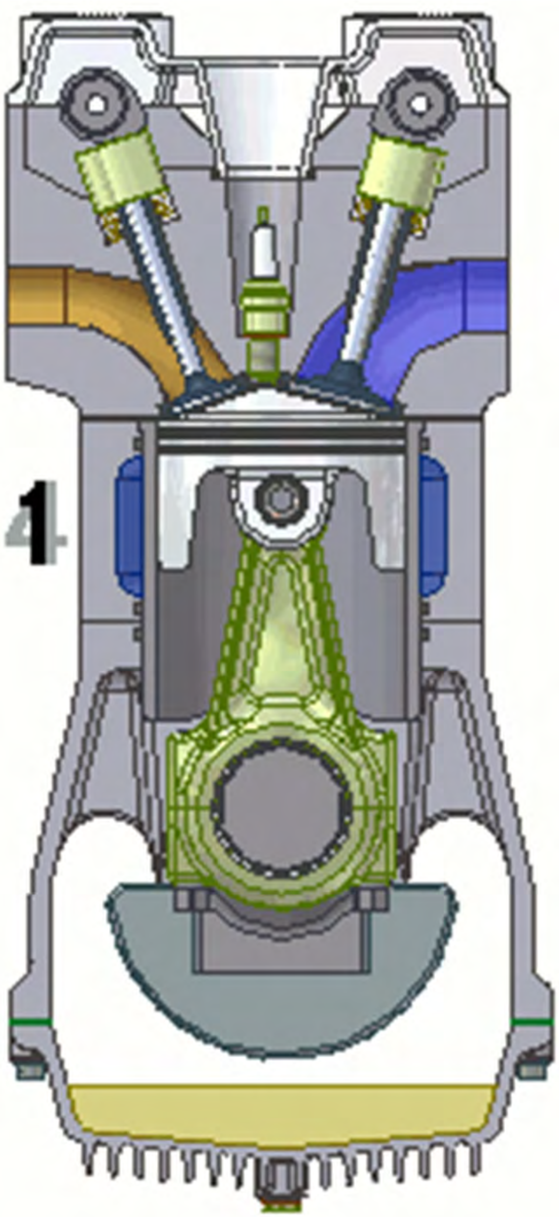


The Otto Cycle for a Heat Engine

An internal combustion engine

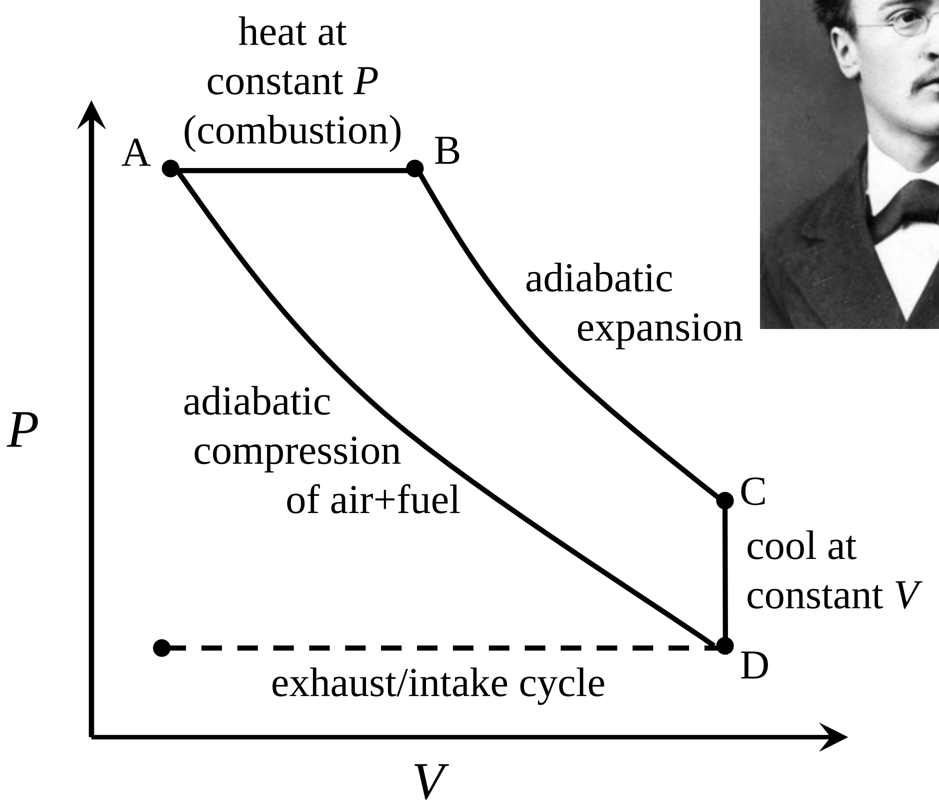


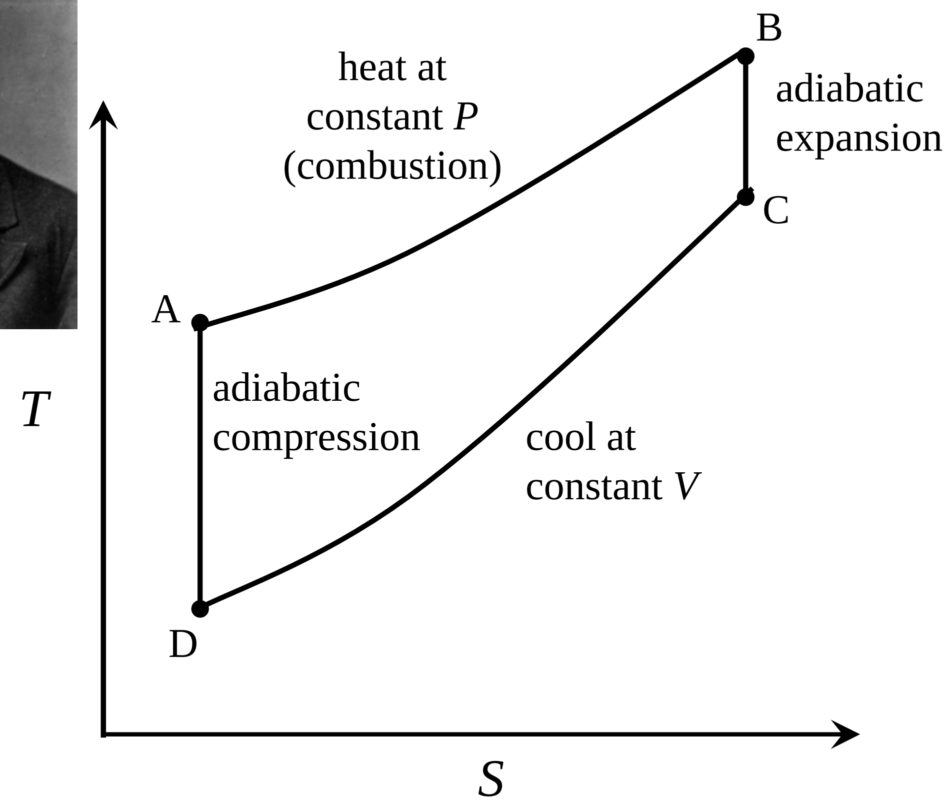
Nicolaus Otto
1832-1891



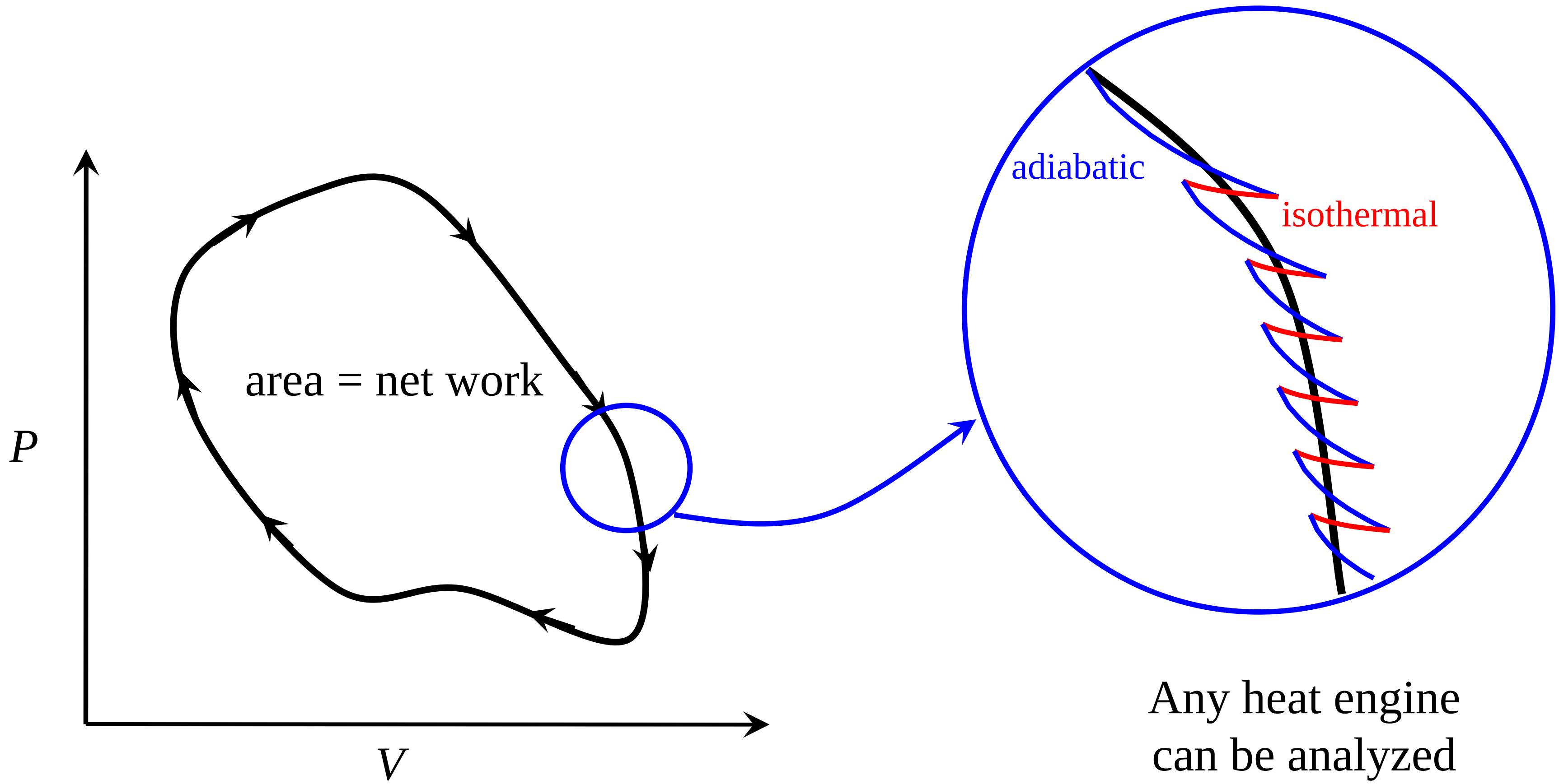
The Diesel Cycle for a Heat Engine

An internal combustion engine - Rudolf Diesel (1858-1913)





Any Cycle for a Heat Engine



Any heat engine
can be analyzed
with the formalism
of the Carnot Cycle.