Energy Systems Engineering

Organization of the course

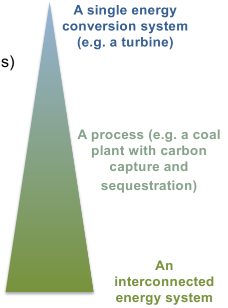
The toolkit:

1 Technical aspects of energy
  - Thermodynamics: 1st and 2nd law
  - Heat to work conversion (T-S diagrams, ideal systems, real systems)
  - Engines
  - Exergy
  - Electrical systems

2 Systems modeling
  - Basic systems modeling
  - Heat integration and pinch analysis
  - Life cycle assessment

3 Process and Energy Economics

Objectives: 1. understand and analyze multi-scale energy processes



Objectives: 2. practice these skills by evaluating a technology

Organization of the course

The toolkit:

Objectives: 1. understand and analyze multi-scale energy processes

1 Technical aspects of energy
  - Thermodynamics: 1st and 2nd law
  - Heat to work conversion (T-S diagrams, ideal systems, real systems)
  - Engines
  - Exergy
  - Electrical systems

2 Systems modeling
  - Basic systems modeling
  - Heat integration and pinch analysis
  - Life cycle assessment

3 Process and Energy Economics

Exam on the lectures (50% of the grade)

Test will be on April 29th and be open book.

Project: evaluation of a technology and its potential (50% of a grade)

Objectives: 2. practice these skills by evaluating a technology

Organization of the course

Weekly organization:

Technical aspects of energy & Systems modeling will cover the first 9 weeks.

This part of the course will be very technical and therefore will feature exercises and be examined with a written midterm test.

During those 9 weeks, there will be no separate exercise session. We will intersperse the exercise within the lecture. Each problem set will typically feature 3-4 exercises. We will usually do 2 exercises in class and you can do 1 exercise independently to check your knowledge.

During the last 4 weeks, there will be no lecture. The assistant will be available to answer questions and help guide you to prepare your project.

Project

Aim: Critical evaluation of a technology (from a patent, an article, a news story…etc.) related to energy or sustainability. You should analyze (qualitatively and quantitatively) whether an idea or technology is feasible (technology scale) and can lead to a scalable solution (system scale) for an energy related issue. What are the bottlenecks? Can these bottlenecks be addressed, etc?

- The project is done in groups of 2-3 (self-assembled)
- Timeline:
  - April 1st: Make the groups, and present and discuss at least 1 proposal for a technology and a source with the assistant
  - April 17th: Submit proposed outline and plan of work
  - May 30th at midnight: Submit report (max 15 pages with figures but not references, 12 font size, no formatting tricks)
  - Week after classes: oral presentation of report + questions (they will be scheduled individually for each group)

Energy Systems Engineering

1. Technical aspects of energy

Outline of Part 1: Thermo

Objective: Derive and understand the physical laws that characterize and limit energy conversion systems

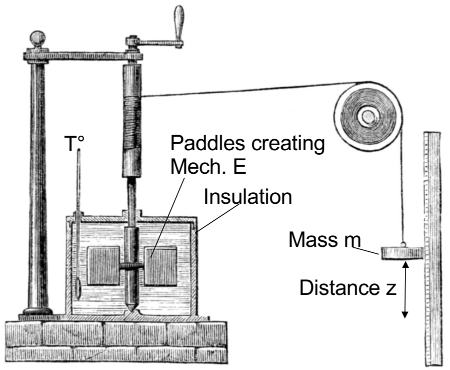
- 1st Law of Thermodynamics
  - Internal energy
  - Work
  - Enthalpy
- 2nd Law of Thermodynamics
  - Entropy
  - Reversible and irreversible processes
  - State functions
- Heat to work conversion
  - T-S diagrams
  - Idealized systems (Carnot cycle)
- Real heat to work and work to heat conversion systems
  - Rankine cycles
  - Refrigeration cycles and heat pumps
  - Engines
- Exergy: calculating the maximum work that can be produced/recovered
- Electrical systems
  - Electrical machines
  - Fuel cells

Literature

- Levenspiel, Octave. 1996. *Understanding Engineering Thermo*. Upper Saddle River, NJ: Prentice Hall.
- Tester, Jefferson W. 2012. *Sustainable Energy: Choosing Among Options*. Cambridge, Mass: MIT Press.

What is energy?

First real answer came during the Joule experiment:



Source: Wikimedia commons

Observation:

$$mgz = mCp\Delta T$$

Therefore, potential energy is entirely recovered as thermal energy

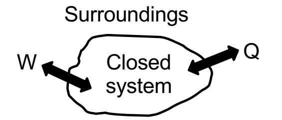
→ **Energy is conserved!**

1st Law of thermodynamics

The observation of a quantity called energy that remains constant = basis for the first law.

Basic energy balance structure for a closed system:

$$Accumulation = In - Out$$



Heat and work (deformable!) can be exchanged with the surroundings but not matter

Change in energy of the system

Work added to the system

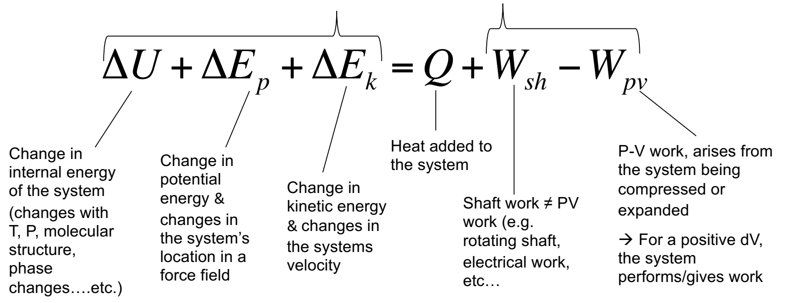
$$\Delta E = Q + W$$

Heat added to the system

1st Law of thermodynamics

Let's further separate these terms into various components:

$$\Delta E = Q + W$$



$$\overbrace{\Delta U + \Delta E_p + \Delta E_k}^{\Delta E} = Q + \overbrace{W_{sh} - W_{pv}}^{W}$$

Change in internal energy of the system (changes with T, P, molecular structure, phase changes….etc.)

Change in potential energy & changes in the system's location in a force field

Change in kinetic energy & changes in the systems velocity

Heat added to the system

Shaft work ≠ PV work (e.g. rotating shaft, electrical work, etc…

P-V work, arises from the system being compressed or expanded

→ For a positive dV, the system performs/gives work

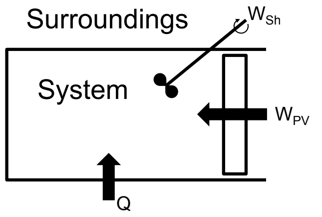
1st Law of thermodynamics

$$\Delta U + \Delta E_p + \Delta E_k = Q + W_{sh} - W_{pv}$$

Let's further simplify this expression :

$$\Delta U = Q + W_{sh} - W_{pv}$$

A simple a closed system:



Pressure volume (PV) work

This is the general form of PV work:

$$W_{PV} = \int_{V_1}^{V_2} P\,dV$$

How do we solve this for a non-constant pressure?

We need P = f(T,V,n) → this is called and equation of state (EOS)

Ideal gas law:

$$PV = nRT \text{ or } P = \frac{n}{V}RT$$

Van der Waals:

$$\left(P + \frac{an^2}{V^2}\right) = \frac{RT}{\left(V/n - b\right)}$$

Enthalpy

Why do we use enthalpy (H) instead of internal energy (U) in most engineering systems?

You have to consider not just internal energy but the volume of the system. To exist, a system has to push back the surroundings.

→ This takes work!

$$W = \int_{0}^{V} P\,dV = PV$$

It is useful to define a quantity (enthalpy, H) that accounts for this work:

$$H = U + PV$$

The 1st law with U and H

In a lot of systems, the pressure is constant, because we live under an atmosphere at constant pressure!

1st Law for a system surrounded by constant pressure:

$$\Delta U = Q + W_{sh} - W_{pv} \rightarrow \Delta U + W_{pv} = \Delta U + P\Delta V = \boxed{\Delta H = Q + W_{sh}}$$

In most engineering systems, this will be a very useful iteration of the 1st Law.

For a system at constant volume:

$$\Delta U = Q + W_{sh}$$

Absolute values for U and H

The absolute value for internal energy (U_0) is given by Einstein's expression:

$$U_0 = E_0 = m_0 C^2 \text{ and } \Delta U = \Delta m C^2$$

Mass changes are so small that this is impractical so in practice the community uses **standard states**.

Often, the standard states is "elements (C, He,…) or di-elements (H_2, O_2…) at 298.15 K and 1 atm" (IUPAC recommends 273.15 K and 10^5 Pa).

This is often impractical for fuel systems (C_x,H_y,O_z). For fuels, it is easier to consider enthalpy as 0 for fully oxidized state (CO_2 and H_2O)

Heating Values

If the fully oxidized state is considered as the reference state. Two potential values can be used for enthalpy:

Lower Heating Value (LHV)	**Higher Heating Value (HHV)**
Combustion products are cooled to 150°C	Combustion products are cooled to 25°C

Both are easy to measure in a bomb calorimeter.

The major difference is water condensation!

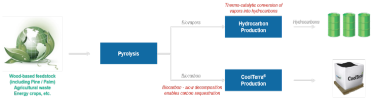
$$LHV \approx HHV - \Delta H_{vap,\ H_2O}\ n_{H_2O}/n_{fuel}$$

Heating Values

Fuel	HHV [MJ/kg]	LHV [MJ/kg]
H_2	142	120
Natural gas	55	49
Gasoline	47	43
Diesel	46	43
Ethanol	30	27
Butanol	37	34
Wood	21	20
Grasses	18	17

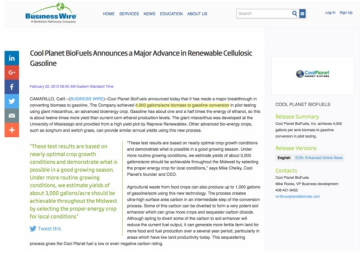
Source: Biomass energy data book, ORNL, 2011

Every few months a new
“miracle technology” appears.



Serious company: investments from BP, Google Ventures, Conoco Phillips…

Claims to produce hydrocarbons and biocarbon.



Cool Planet BioFuels Announces a Major Advance in Renewable Cellulosic Gasoline

February 22, 2012 09:00 AM Eastern Standard Time

CAMARILLO, Calif.--(BUSINESS WIRE)--Cool Planet BioFuels announced today that it has made a major breakthrough in converting biomass to gasoline. The Company achieved 4,000 gallons/acre biomass to gasoline conversion in pilot testing using giant miscanthus, an advanced bioenergy crop. Gasoline has about one and a half times the energy of ethanol, so this is about twelve times more yield than current corn ethanol production levels. The giant miscanthus was developed at the University of Mississippi and provided from a high yield plot by Repreve Renewables. Other advanced bio-energy crops, such as sorghum and switch grass, can provide similar annual yields using this new process.

“These test results are based on nearly optimal crop growth conditions and demonstrate what is possible in a good growing season. Under more routine growing conditions, we estimate yields of about 3,000 gallons/acre should be achievable throughout the Midwest by selecting the proper energy crop for local conditions”

“These test results are based on nearly optimal crop growth conditions and demonstrate what is possible in a good growing season. Under more routine growing conditions, we estimate yields of about 3,000 gallons/acre should be achievable throughout the Midwest by selecting the proper energy crop for local conditions,” says Mike Cheiky, Cool Planet's founder and CEO.

Agricultural waste from food crops can also produce up to 1,000 gallons of gasoline/acre using this new technology. The process creates ultra-high surface area carbon in an intermediate step of the conversion process. Some of this carbon can be diverted to form a very potent soil enhancer which can grow more crops and sequester carbon dioxide. Although opting to divert some of the carbon to soil enhancer will reduce the current fuel output, it can generate more fertile farm land for more food and fuel production over a several year period, particularly in areas which have low land productivity today. This sequestering process gives the Cool Planet fuel a low or even negative carbon rating.

COOL PLANET BIOFUELS

Release Summary

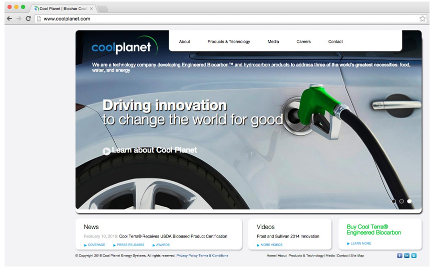
Cool Planet BioFuels, Inc. achieves 4,000 gallons per acre biomass to gasoline conversion in pilot testing.

Release Versions

English EON: Enhanced Online News

Contacts

Cool Planet BioFuels
Mike Rocke, VP Business development
408-421-9455
mr@coolplanetbiofuels.com



We are a technology company developing Engineered Biocarbon™ and hydrocarbon products to address three of the world's greatest necessities: food, water, and energy

News

February 10, 2016: Cool Terra® Receives USDA Biobased Product Certification

Videos

Frost and Sullivan 2014 Innovation

Buy Cool Terra® Engineered Biocarbon

© Copyright 2016 Cool Planet Energy Systems. All rights reserved. Privacy Policy Terms & Conditions

Impressive number: **3000-4000 gallons/acre gasoline**

Should you invest?

This was a real question that William Banholzer got when he was CEO of Dow Chemical.

Hint: Let’s use the first law to calculate the absolute minimum amount of biomass that would require and see if it is a realistic amount to expect from one acre…

Outline of Part 1: Thermo

Objective: Derive and understand the physical laws that characterize and limit energy conversion systems

- 1st Law of Thermodynamics
  - Internal energy
  - Work
  - Enthalpy
- **2nd Law of Thermodynamics**
  - Entropy
  - Reversible and irreversible processes
  - State functions
- Heat to work conversion
  - T-S diagrams
  - Idealized systems (Carnot cycle)
- Real heat to work and work to heat conversion systems
  - Rankine cycles
  - Refrigeration cycles and heat pumps
  - Engines
- Exergy: calculating the maximum work that can be produced/recovered
- Electrical systems
  - Electrical machines
  - Fuel cells

Entropy

Entropy: measure of system disorder or total inventory of random information.

The second law of thermodynamics is based around entropy. It states:

$$\Delta S_{system} \geq 0$$

This expression is true for isolated systems. For non-isolated systems, we have:

$$\Delta S_{system} + \Delta S_{surroundings} \geq 0$$

$\Delta S = 0 \Rightarrow$ **Reversible process**

Entropy

How is entropy measured?

$$\Delta S_{system} = S_2 - S_1 = \int_{S_1}^{S_2} \frac{dQ_{rev}}{T}$$

Since the change is reversible the total entropy change is zero but the system's entropy can still increase:

$$\Delta S_{system,rev} + \Delta S_{surroundings,rev} = 0$$

Reversible processes

What does a reversible process look like?

$$\Delta S = 0 \longrightarrow \text{Equilibrium}$$

For a reversible process, there is no change in entropy and therefore the system is at equilibrium. This means:

- No Gradients (temperature, mass, flow…etc.)
- No mechanical losses through heat dissipation
- …

Achieving this would require **infinitesimal changes infinitely slowly**
→ **Impossible**

State functions

$$S_2 - S_1 = \int_{S_1}^{S_2} \frac{dQ_{rev}}{T}$$

If reversible processes are impossible to achieve, how is ΔS calculated?

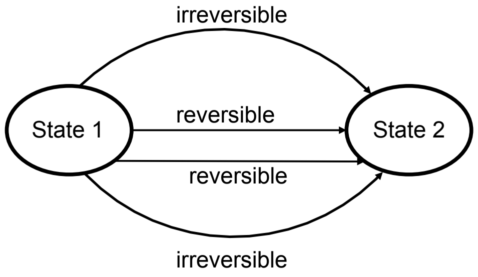
Fortunately, S (similarly to U, H or G) is a **state function**. This means that these variables:

- Characterize a system at equilibrium
- Have no “memory”
  - → Are independent of the path taken to reach their state

The existence of these state variable is a fundamental postulate in thermodynamics.

State functions

To calculate the change in a state variable, we can use any path we want:



For each state change, there will be an infinite number of paths.

→ To calculate a change in S (or another state variable) we can use a "virtual" path that is a *reversible* one.

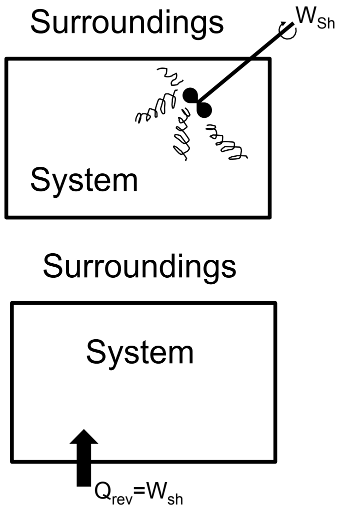
Example

1 kg of water at 20°C, stirred by a stirrer (4184 J_e are used) in a perfectly insulated system.

Mechanical energy is dissipated as heat, which heats the water to 21°C

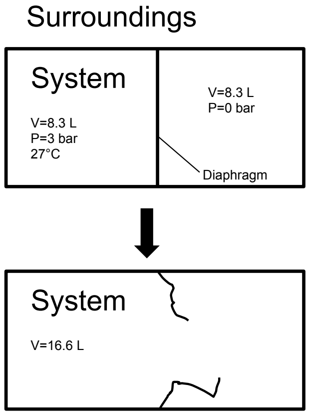
This is a highly irreversible process!

Can we find a path that gets us to the same state?



Problem 2

Assume we have a perfectly isolated system with 1 mole of an ideal gas at a pressure P = 3 bar in a 16.6 L chamber that is isolated by a diaphragm from another 16.6 L chamber that has been evacuated. What is the change in entropy?



Reminder: for an ideal gas U=f(T) only and U ≠ f(p,V)

Outline of Part 1: Thermo

Objective: Derive and understand the physical laws that characterize and limit energy conversion systems

- 1^{st} Law of Thermodynamics
  - Internal energy
  - Work
  - Enthalpy
- 2^{nd} Law of Thermodynamics
  - Entropy
  - Reversible and irreversible processes
  - State functions
- **Heat to work conversion**
  - T-S diagrams
  - Idealized systems (Carnot cycle)
- Real heat to work and work to heat conversion systems
  - Rankine cycles
  - Refrigeration cycles and heat pumps
  - Engines
- Exergy: calculating the maximum work that can be produced/recovered
- Electrical systems
  - Electrical machines
  - Fuel cells

State functions and work

Why are state functions particularly relevant to generating work?

Many processes are cyclical/steady state.

Living organisms

Engines

Gas turbine

Etc…

Heat to work!

Since they return to the same state, they can all be characterized by state variables!

Heat to work and entropy

For heat to work cyclical processes, entropy is an interesting state variable for characterizing the system:

Recall the definition of entropy:

$$dS = \frac{dQ_{rev}}{T}$$

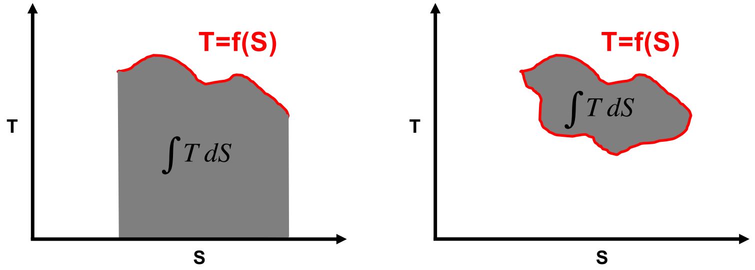
This definition links entropy to Q_{rev} and Q_{rev} is the greatest amount of heat that can be received for a given change in entropy.

Heat to work and entropy

If we integrate, we can get the total amount of reversible heat exchanged:

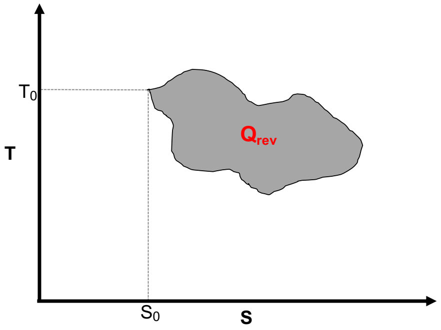
$$Q_{rev} = \int T\,dS$$

What does an integral actually mean?



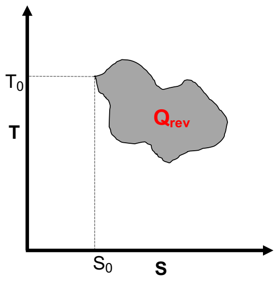
Heat to work and entropy

The area represents reversible heat:



$$dS > \frac{dQ_{actual}}{T} \longrightarrow Q_{actual} < \int T\,dS$$

Heat to work and entropy



1^{st} law:

$$\Delta U = Q + W$$

For a cycle:

$$\Delta U = 0$$ U is a State variable!

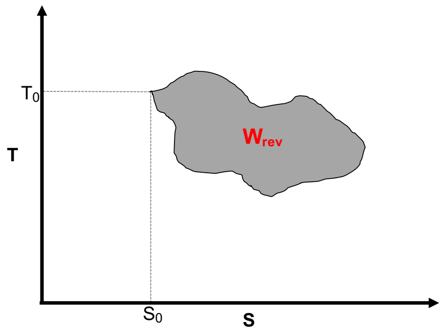
$$\longrightarrow \quad Q = -W$$

This is true for any cycle. Therefore, for a reversible cycle, we have:

$$Q_{rev} = -W_{rev}$$

Heat to work and entropy

The area represents reversible work as well:



$$W_{actual} = -Q_{actual} < -\int T\, dS$$

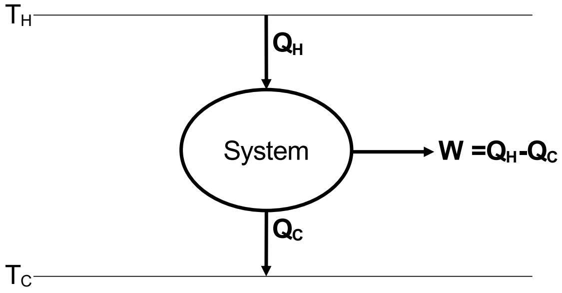
T-S cycles

What we know:

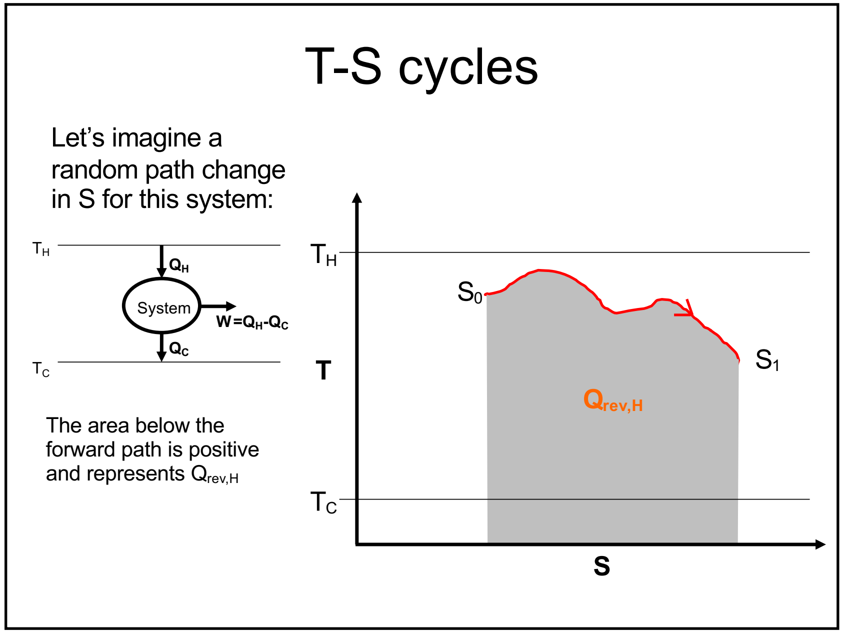
- A thermodynamic cycle can produce work
- The cycle can be represented on a T-S diagram
- The area of the cycle represents the maximum/reversible work that can be obtained

What do you need for a real cycle to function?

T-S cycles



The hot and cold source are the key to an engine!

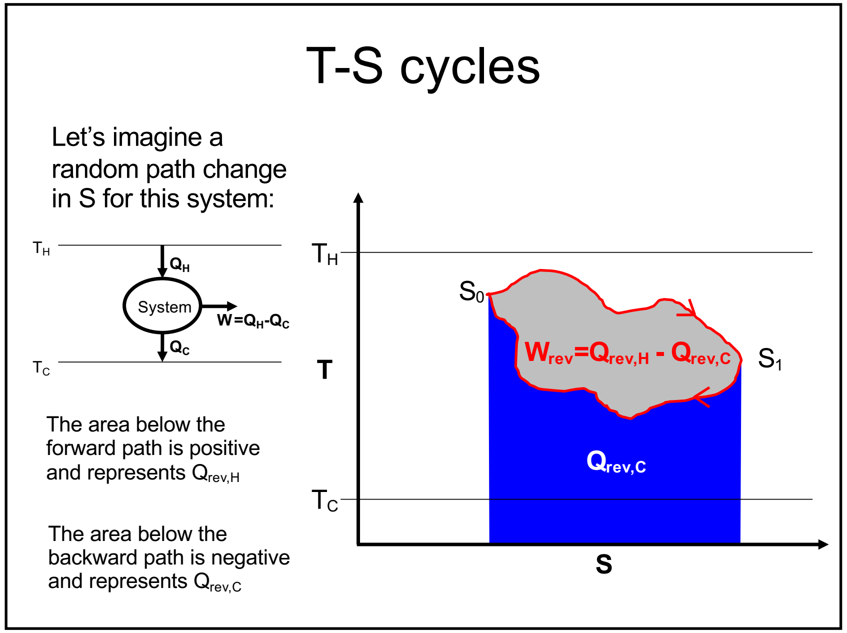


T-S cycles

Let's imagine a random path change in S for this system:

The area below the forward path is positive and represents $Q_{rev,H}$

37



T-S cycles

Let's imagine a random path change in S for this system:

The area below the forward path is positive and represents $Q_{rev,H}$

The area below the backward path is negative and represents $Q_{rev,C}$

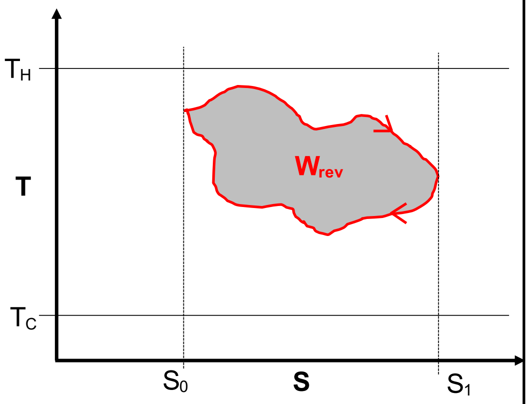
38

T-S cycles

For a random cycle delimited by T_H, T_C, S_0 and S_1:

$W_{max} = W_{rev}$

What is the cycle with the maximum efficiency?



Efficiency:

$$\eta = \frac{W}{Q_H}$$

Thermo Recap

In order to analyze this system for ideal gases, we will need some relations for ideal gases. Let's derive them…

Starting point, for ideal gases: $U = f(T) \neq f(P,V)$ (this postulate is part of what defines ideal gases)

Therefore, we can define: $dU = C_V dT \rightarrow \Delta U = C_V \Delta T$ (always true for ideal gases)

Similarly, we define: $\Delta H = C_P \Delta T$

Heat capacity (at constant volume C_V or at constant pressure C_P)

With the definition of *H*: $\Delta U = C_V \Delta T = \Delta H - \Delta(PV) = C_P \Delta T - \Delta(RT)$

$\rightarrow C_P - C_V = R\Delta T / \Delta T = R$

It is useful to define *k*: $k = C_P / C_V = R / C_V + 1$

Thermo Recap

With this definition, we can derive relations for an adiabatic process (*dQ=0*):

$$dU = C_V dT = dW = -pdV = -\frac{RT}{V}dV$$

Let's separate and integrate:

$$\ln\left(\frac{T_2}{T_1}\right) = -\frac{R}{C_V}\ln\left(\frac{V_2}{V_1}\right) = -(k-1)\ln\left(\frac{V_2}{V_1}\right) \rightarrow \left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{k-1}$$

With *V=RT/P*:

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{T_1P_2}{T_2P_1}\right)^{k-1} \rightarrow \left(\frac{T_2}{T_1}\right)^{1+k-1} = \left(\frac{P_2}{P_1}\right)^{k-1} \rightarrow \left(\frac{T_2}{T_1}\right) = \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}}$$

Combining both expression:

$$\left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}} = \left(\frac{V_1}{V_2}\right)^{k-1} \rightarrow \left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^{k}$$

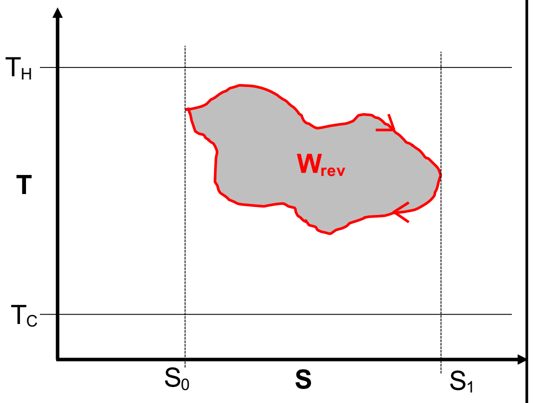
These 3 expressions along with $C_V dT = -pdV$ will be useful when describing adiabatic processes for ideal gases…

T-S cycles

For a random cycle delimited by T_H, T_C, S_0 and S_1:

$W_{max} = W_{rev}$

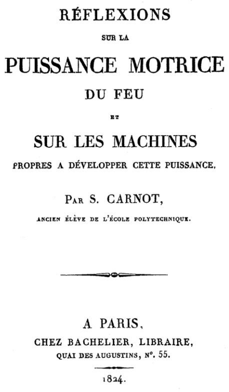
What is the cycle with the maximum efficiency?



Efficiency:

$$\eta = \frac{W}{Q_H}$$

Carnot



RÉFLEXIONS
SUR LA
PUISSANCE MOTRICE
DU FEU
ET
SUR LES MACHINES
PROPRES A DÉVELOPPER CETTE PUISSANCE.

PAR S. CARNOT,
ANCIEN ÉLÈVE DE L'ÉCOLE POLYTECHNIQUE.

A PARIS,
CHEZ BACHELIER, LIBRAIRE,
QUAI DES AUGUSTINS, N°. 55.

1824.

Carnot's main points

His motivations

Growing importance of machines

L'étude de ces machines est du plus haut intérêt, leur importance est immense, leur emploi s'accroît tous les jours. Elles paraissent destinées à produire une grande révolution dans le monde civilisé.

Key thermodynamic concepts

Heat sources/sinks at T_H and T_C

La production de la puissance motrice est donc due, dans les machines à vapeur, non à une consommation réelle du calorique, *mais à son transport d'un corps chaud à un corps froid*

Partout où il existe une différence de température, il peut y avoir production de puissance motrice.

No unnecessary entropy changes

La condition nécessaire du maximum est donc *qu'il ne se fasse dans les corps employés à réaliser la puissance motrice de la chaleur aucun changement de température qui ne soit dû à un changement de volume.*

His obsession with the British

Enlever aujourd'hui à l'Angleterre ses machines à vapeur, ce serait lui ôter à la fois la houille et le fer; ce serait tarir toutes ses sources de richesses, ruiner tous ses moyens de prospérité; ce serait anéantir cette puissance colossale. La destruction de sa marine, qu'elle regarde comme son plus ferme appui, lui serait peut-être moins funeste.

Maximum of engine efficiency

Quel est ici le sens du mot *maximum?*

le *maximum de puissance motrice résultant de l'emploi de la vapeur est aussi le maximum de puissance motrice réalisable par quelque moyen que ce soit.*

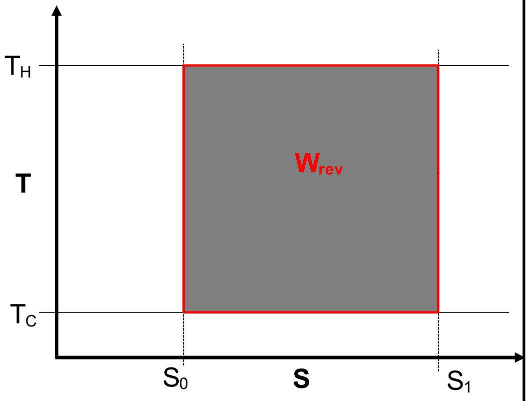
La puissance motrice de la chaleur est indépendante des agens mis en œuvre pour la réaliser; sa quantité est fixée uniquement par les températures des corps entre lesquels se fait en dernier résultat le transport du calorique.

The Carnot cycle

Recall our question:

What is the cycle with the maximum efficiency?

$$\eta = \frac{W}{Q_H}$$



No more T-differences!

Sustainable Energy Systems

1. Technical aspects of energy

Outline of Part 1: Thermo

Objective: Derive and understand the physical laws that characterize and limit energy conversion systems

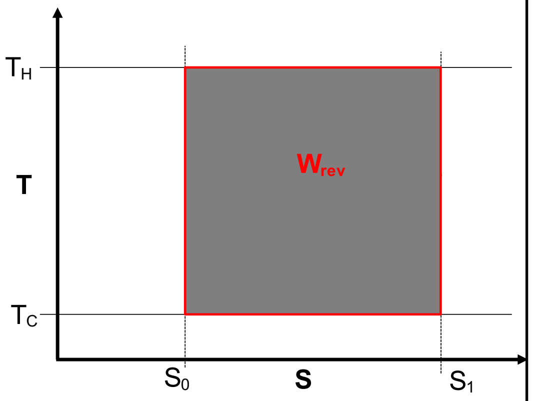
- 1st Law of Thermodynamics
  - Internal energy
  - Work
  - Enthalpy
- 2nd Law of Thermodynamics
  - Entropy
  - Reversible and irreversible processes
  - State functions
- Heat to work conversion
  - T-S diagrams
  - **Idealized systems (Carnot cycle)**
- Real heat to work and work to heat conversion systems
  - Rankine cycles
  - Refrigeration cycles and heat pumps
  - Engines
- Exergy: calculating the maximum work that can be produced/recovered
- Electrical systems
  - Electrical machines
  - Fuel cells

The Carnot cycle

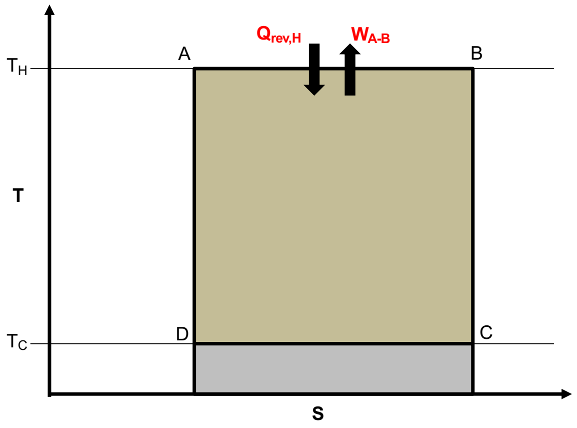
Recall our question:

What is the cycle with the maximum efficiency?

$$\eta = \frac{W}{Q_H}$$



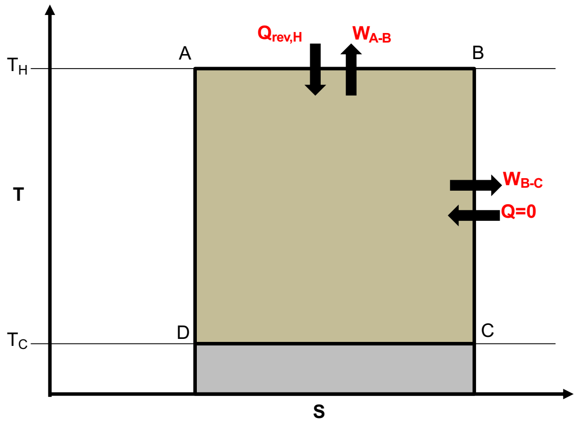
The Carnot cycle



Step A-B:

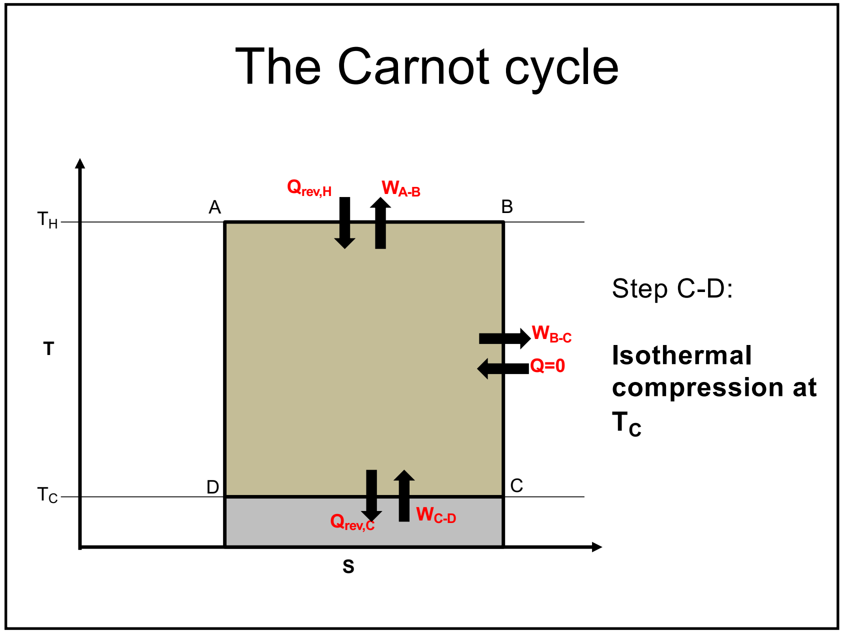
Isothermal expansion at T_H

The Carnot cycle



Step B-C:

Adiabatic expansion from T_H to T_C

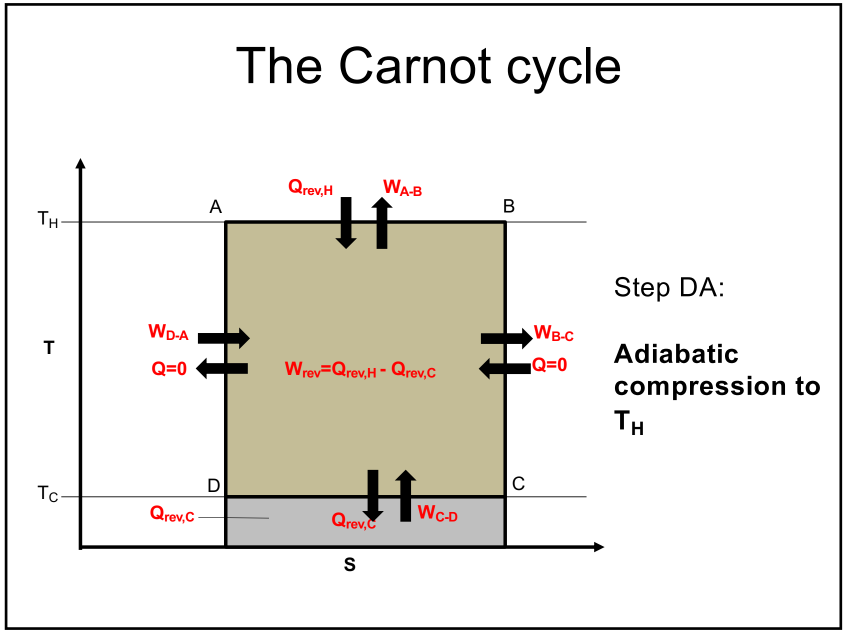


The Carnot cycle

Step C-D:

Isothermal compression at T_C

51



The Carnot cycle

Step DA:

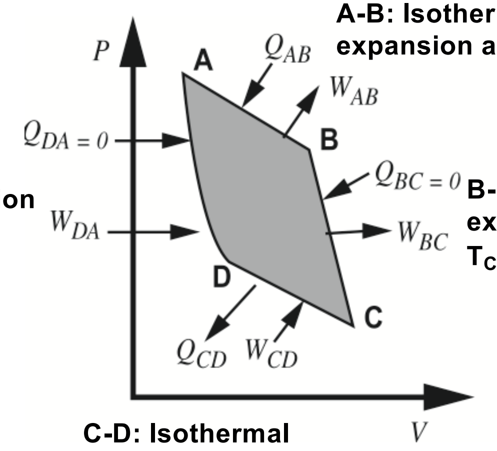
Adiabatic compression to T_H

52

The Carnot cycle

A-B: Isothermal expansion at T_H

D-A: Adiabatic compression to T_H

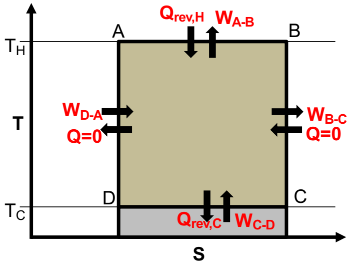


B-C: Adiabatic expansion to T_C

C-D: Isothermal compression at T_C

The Carnot cycle

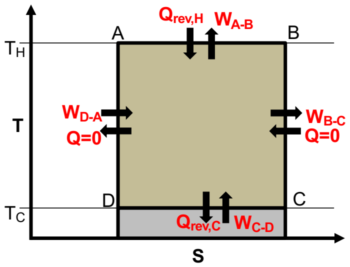
What is the maximum efficiency?



$$\eta = \frac{W}{Q_H}$$

$$\eta = \frac{W}{Q_H} = \frac{-W_{tot}}{Q_{AB}} = \frac{-(W_{AB} + W_{BC} + W_{CD} + W_{DA})}{Q_{AB}}$$

The Carnot cycle



Step A-B: Isothermal expansion

T= cst U=f(T)≠f(P,V) for ideal gases:

$$\Delta U = Q + W = 0 \;\rightarrow\; Q_{AB} = -W_{AB}$$

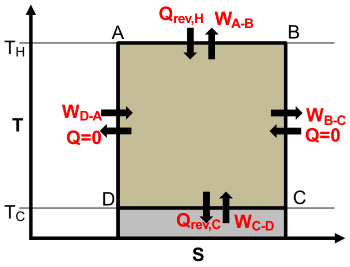
$$= \int p\,dV = RT_H \int \frac{dV}{V} =$$

$$RT_H \ln\frac{V_B}{V_A} = RT_H \ln\frac{P_A}{P_B}$$

Step A-B

$$Q_{AB} = -W_{AB} =$$
$$RT_H \ln\frac{P_A}{P_B}$$

The Carnot cycle



Step B-C: Adiabatic expansion

U=f(T) and Cv=cst (for ideal gases):

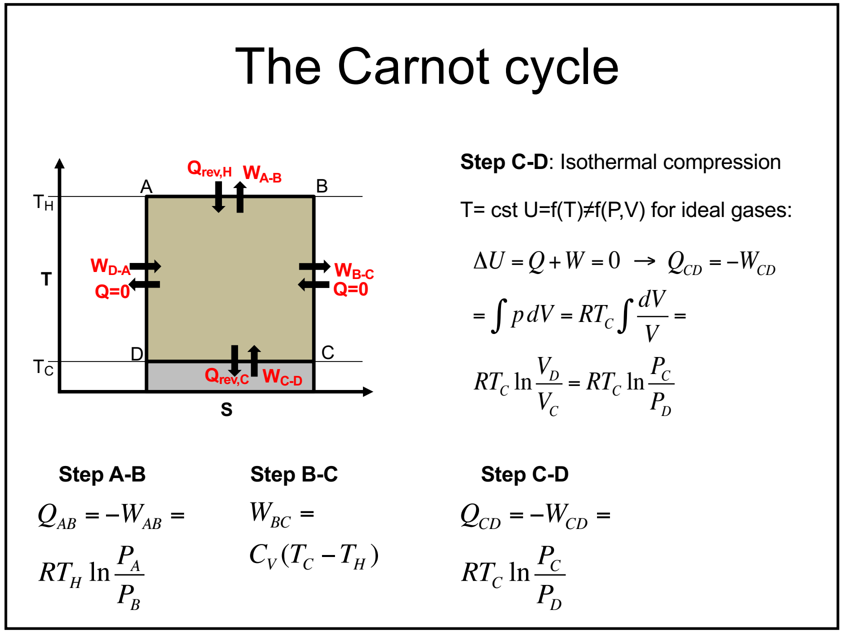
$$\Delta U = Q + W = W_{BC} =$$
$$C_V \Delta T = C_V (T_C - T_H)$$

Step A-B

$$Q_{AB} = -W_{AB} =$$
$$RT_H \ln\frac{P_A}{P_B}$$

Step B-C

$$W_{BC} =$$
$$C_V (T_C - T_H)$$



The Carnot cycle

Step C-D: Isothermal compression

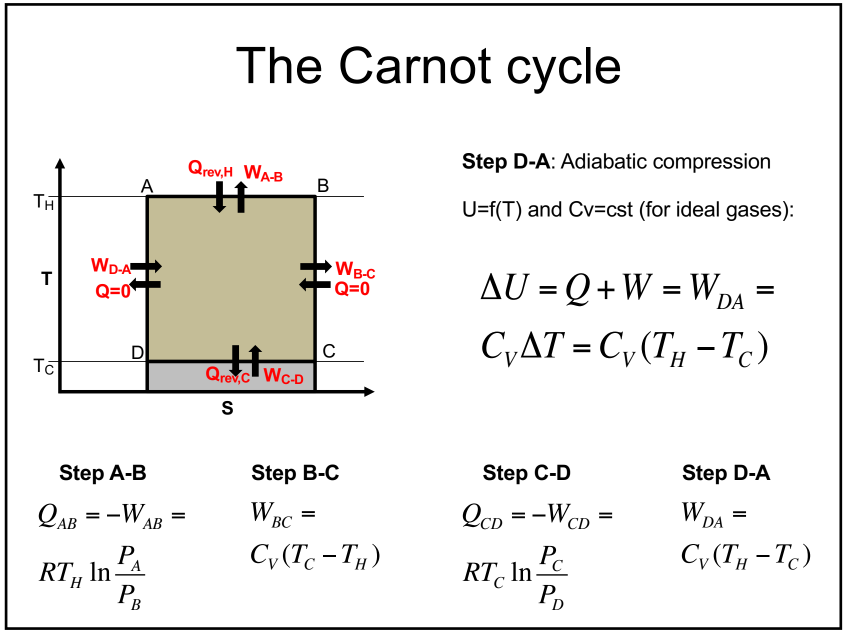
T= cst U=f(T)≠f(P,V) for ideal gases:

$$\Delta U = Q + W = 0 \;\rightarrow\; Q_{CD} = -W_{CD}$$

$$= \int p\,dV = RT_C \int \frac{dV}{V} =$$

$$RT_C \ln\frac{V_D}{V_C} = RT_C \ln\frac{P_C}{P_D}$$

Step A-B	**Step B-C**	**Step C-D**
$Q_{AB} = -W_{AB} =$	$W_{BC} =$	$Q_{CD} = -W_{CD} =$
$RT_H \ln\frac{P_A}{P_B}$	$C_V(T_C - T_H)$	$RT_C \ln\frac{P_C}{P_D}$



The Carnot cycle

Step D-A: Adiabatic compression

U=f(T) and Cv=cst (for ideal gases):

$$\Delta U = Q + W = W_{DA} =$$

$$C_V \Delta T = C_V (T_H - T_C)$$

Step A-B	**Step B-C**	**Step C-D**	**Step D-A**
$Q_{AB} = -W_{AB} =$	$W_{BC} =$	$Q_{CD} = -W_{CD} =$	$W_{DA} =$
$RT_H \ln\frac{P_A}{P_B}$	$C_V(T_C - T_H)$	$RT_C \ln\frac{P_C}{P_D}$	$C_V(T_H - T_C)$

The Carnot cycle

Step A-B

$$Q_{AB} = -W_{AB} = RT_H \ln\frac{P_A}{P_B}$$

Step B-C

$$\cancel{W_{BC} = C_V(T_C - T_H)}$$

Step C-D

$$Q_{CD} = -W_{CD} = RT_C \ln\frac{P_C}{P_D}$$

Step D-A

$$\cancel{W_{DA} = C_V(T_H - T_C)}$$

$$\eta = \frac{-W_{tot}}{Q_H} = \frac{-(W_{AB} + W_{BC} + W_{CD} + W_{DA})}{Q_{AB}} = \frac{-W_{AB} - W_{CD}}{Q_{AB}}$$

$$\eta = \frac{RT_H \ln\frac{P_A}{P_B} + RT_C \ln\frac{P_C}{P_D}}{RT_H \ln\frac{P_A}{P_B}}$$

The Carnot cycle

$$\eta = \frac{-W_{tot}}{Q_H} = \frac{RT_H \ln\frac{P_A}{P_B} + RT_C \ln\frac{P_C}{P_D}}{RT_H \ln\frac{P_A}{P_B}} = \frac{T_H \ln\frac{P_A}{P_B} + T_C \ln\frac{P_C}{P_D}}{T_H \ln\frac{P_A}{P_B}}$$

For ideal gases we saw that for an adiabatic step:

$$\left(\frac{P_{final}}{P_{initial}}\right)^{\frac{k-1}{k}} = \left(\frac{T_{final}}{T_{initial}}\right)$$

In our case for both adiabatic steps (A-D and B-C), we have the same interval T_H and T_C:

$$\left(\frac{P_A}{P_D}\right)^{\frac{k-1}{k}} = \left(\frac{T_H}{T_C}\right) = \left(\frac{P_B}{P_C}\right)^{\frac{k-1}{k}}$$

$$\Rightarrow \frac{P_A}{P_D} = \frac{P_B}{P_C} \Rightarrow \frac{P_A}{P_B} = \frac{P_D}{P_C}$$

The Carnot cycle

$$\eta = \frac{-W_{tot}}{Q_H} = \frac{RT_H \ln\frac{P_A}{P_B} + RT_C \ln\frac{P_C}{P_D}}{RT_H \ln\frac{P_A}{P_B}} = \frac{T_H \ln\frac{P_A}{P_B} + T_C \ln\frac{P_B}{P_A}}{T_H \ln\frac{P_A}{P_B}}$$

This results in:

$$\eta = \frac{T_H - T_C}{T_H}$$

The theoretical efficiency of heat to work engines is not 100% unless you can reach infinite temperatures or 0 K!

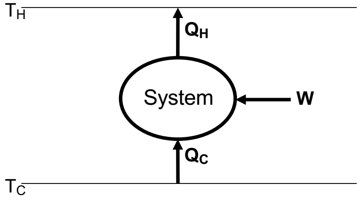
The Carnot heat pump

Sometimes it is useful to use work to move heat from a cold to a hot source

(for the reverse, you don't need work, it happens on its own)

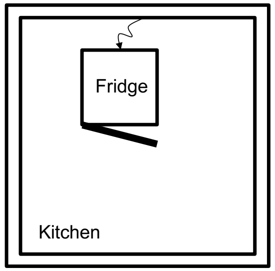
Such systems include:

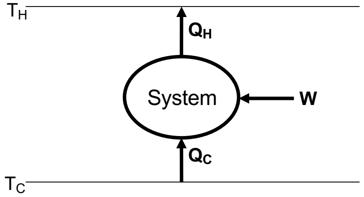
- Refrigerators
- Heat pumps
- Air conditioners



The refrigerator question

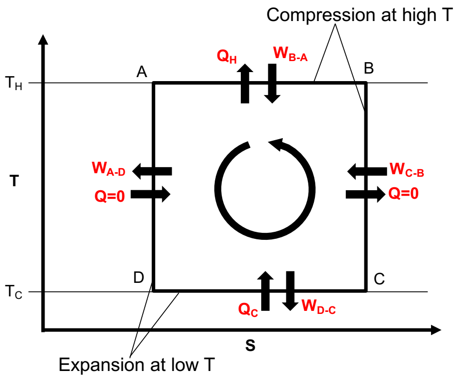
What happens if you leave for the weekend, close the door of your perfectly insulated kitchen but inadvertently leave the refrigerator door open? Does the temperature of the kitchen increase or decrease?

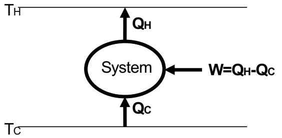




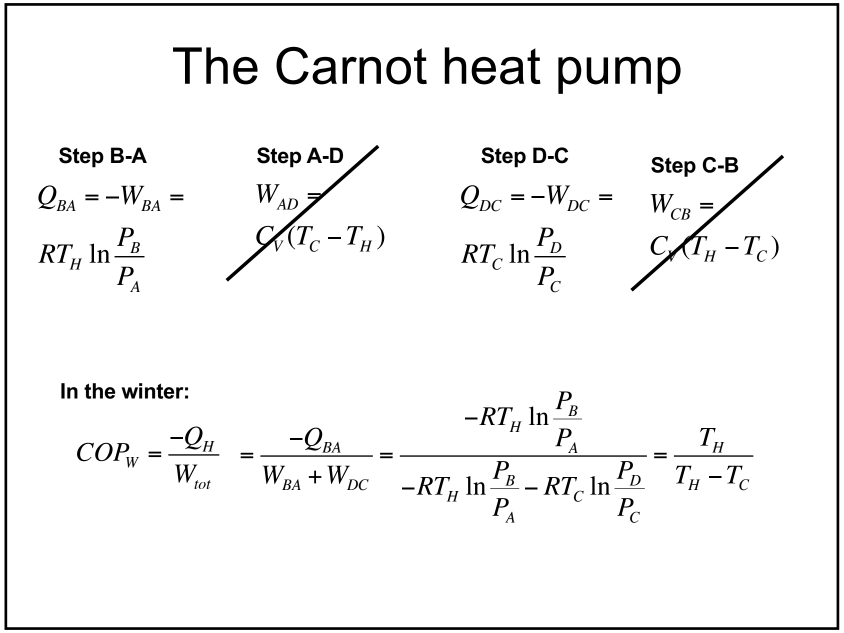
The temperature increases!

The Carnot heat pump





It's simply a Carnot Cycle in reverse!



The Carnot heat pump

Step B-A

$$Q_{BA} = -W_{BA} = RT_H \ln\frac{P_B}{P_A}$$

Step A-D

$$\cancel{W_{AD} = C_V(T_C - T_H)}$$

Step D-C

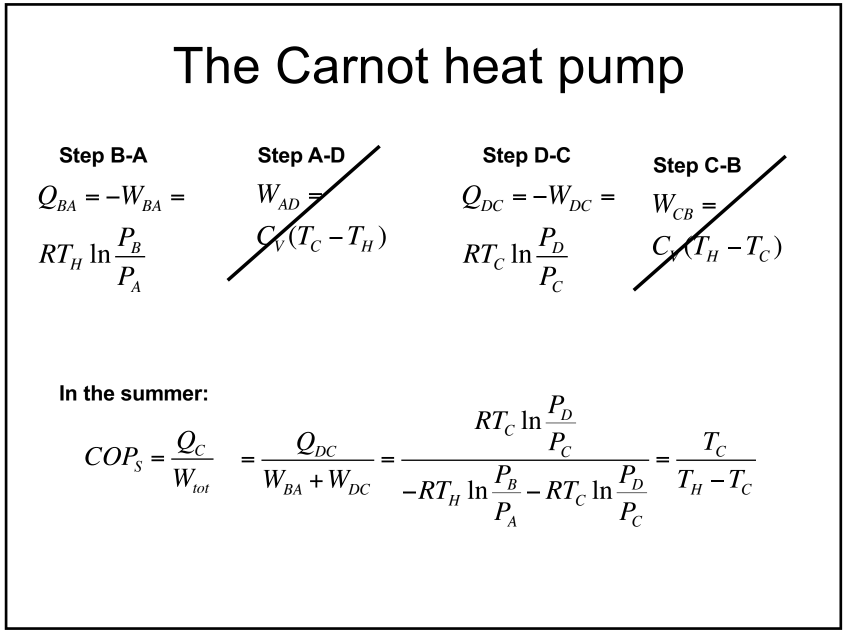
$$Q_{DC} = -W_{DC} = RT_C \ln\frac{P_D}{P_C}$$

Step C-B

$$\cancel{W_{CB} = C_V(T_H - T_C)}$$

In the winter:

$$COP_W = \frac{-Q_H}{W_{tot}} = \frac{-Q_{BA}}{W_{BA} + W_{DC}} = \frac{-RT_H \ln\frac{P_B}{P_A}}{-RT_H \ln\frac{P_B}{P_A} - RT_C \ln\frac{P_D}{P_C}} = \frac{T_H}{T_H - T_C}$$



The Carnot heat pump

Step B-A

$$Q_{BA} = -W_{BA} = RT_H \ln\frac{P_B}{P_A}$$

Step A-D

$$\cancel{W_{AD} = C_V(T_C - T_H)}$$

Step D-C

$$Q_{DC} = -W_{DC} = RT_C \ln\frac{P_D}{P_C}$$

Step C-B

$$\cancel{W_{CB} = C_V(T_H - T_C)}$$

In the summer:

$$COP_S = \frac{Q_C}{W_{tot}} = \frac{Q_{DC}}{W_{BA} + W_{DC}} = \frac{RT_C \ln\frac{P_D}{P_C}}{-RT_H \ln\frac{P_B}{P_A} - RT_C \ln\frac{P_D}{P_C}} = \frac{T_C}{T_H - T_C}$$

ChE-304 Problem Set 2

Week 2

Problem 1

Should I heat my house with a Carnot heat pump or an electric heater? Electric heaters are very efficient. ~100% of the electrical work ends up as heat in the house.
I would like to heat my house to 24°C and the temperature outside in the winter is, on average -4°C.

Outline of Part 1: Thermo

Objective: Derive and understand the physical laws that characterize and limit energy conversion systems

- 1st Law of Thermodynamics
  - Internal energy
  - Work
  - Enthalpy
- 2nd Law of Thermodynamics
  - Entropy
  - Reversible and irreversible processes
  - State functions
- Heat to work conversion
  - T-S diagrams
  - Idealized systems (Carnot cycle)
- **Real heat to work and work to heat conversion systems**
  - Rankine cycles
  - Refrigeration cycles and heat pumps
  - Engines
- Exergy: calculating the maximum work that can be produced/recovered
- Electrical systems
  - Electrical machines
  - Fuel cells

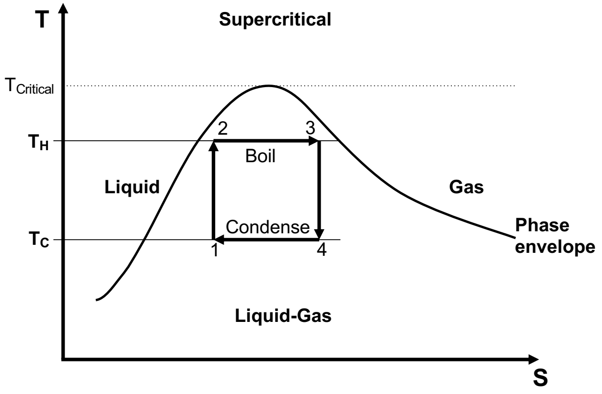
Rankine cycles

The Carnot cycle achieves the highest efficiency but this cycle (or even a close imitation of it) is not practical for several reasons:

- **Steps are impractical (probably impossible to implement)**
- Heat exchanges require (often significant) temperature differences
- Use of a gas compressor instead of a liquid pump at low P (more expensive and less efficient)
- Higher P are required for gases

Water/steam is actually quite attractive for these particular applications!

Rankine cycles



Rankine cycles

Problem: pumping and expansion with phase changes

- Pumping a liquid close to a gaseous state leads to cavitation
- Expanding a gas-to-liquid mixture leads to erosion
- Efficiency losses with formation of droplets
- Pumping a liquid is more efficient than a gas

Pumps and turbines (e.g. devices with moving elements) must be run outside of the 2-phase region

You also want to pump a liquid rather than a gas.

Rankine cycles

Cavitation damage

Turbine blades

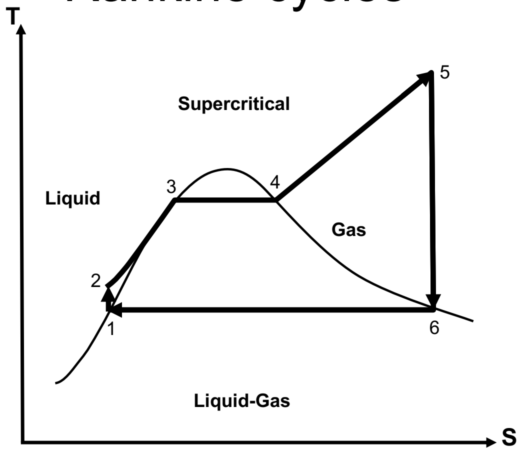
Pump plate

Droplet corrosion damage

Turbine blades

Source: Wikicommons media, http://500daysoficeland.com

Rankine cycles



Step 1-2
Liquid pumping:
Adiabatic
compression

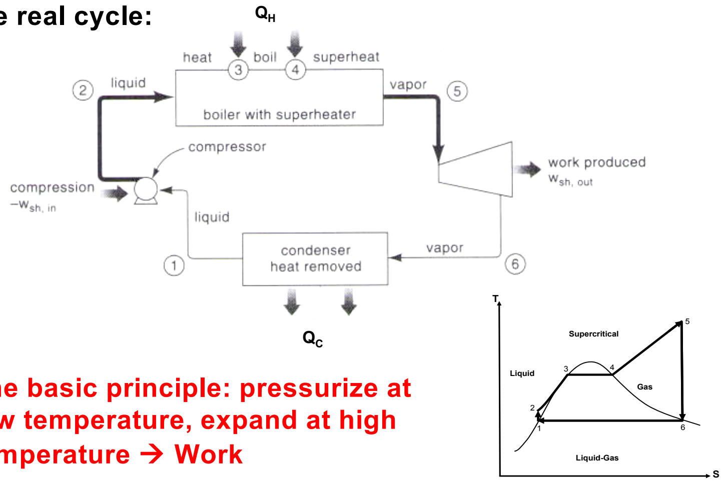
Step 2-3, 3-4, 4-5
Heating of a:
2-3: liquid
3-4: gas-liquid
4-5: gas

Step 5-6
Gas expansion:
Adiabatic
expansion

Step 6-1
Cooling of a gas/liquid

Rankine cycles

The real cycle:

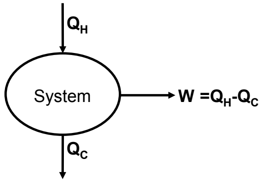


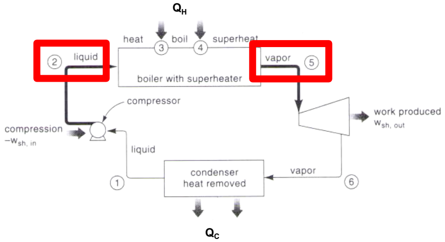
The basic principle: pressurize at low temperature, expand at high temperature → Work

Rankine cycles

Calculating efficiencies:

This view is still accurate:





The efficiency is still:

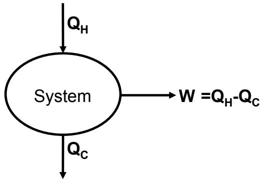
With enthalpy:

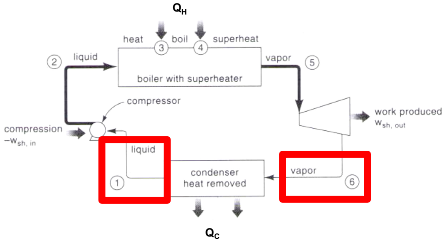
$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = \frac{\boxed{(H_5 - H_2)} - (H_6 - H_1)}{(H_5 - H_2)}$$

Rankine cycles

Calculating efficiencies:

This view is still accurate:





The efficiency is still:

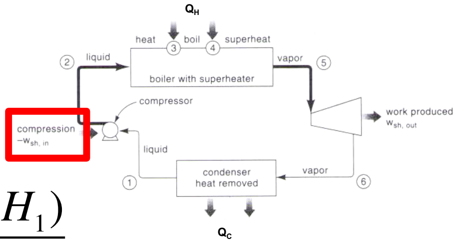
With enthalpy:

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = \frac{(H_5 - H_2) - \boxed{(H_6 - H_1)}}{(H_5 - H_2)}$$

Rankine cycles

Calculating efficiencies:

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H}$$



$$= \frac{(H_5 - H_2) - (H_6 - H_1)}{(H_5 - H_2)}$$

Because the energy for compressing a liquid is small:

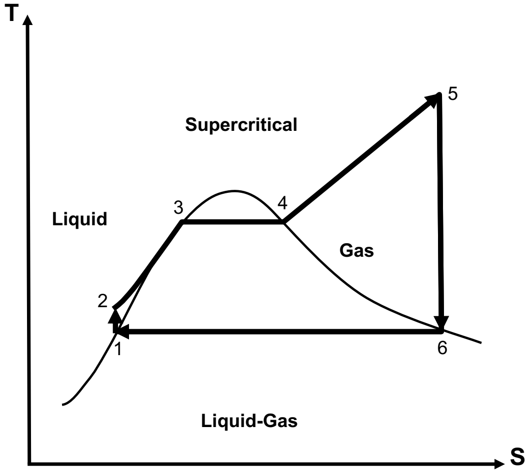
$$H_1 \approx H_2$$

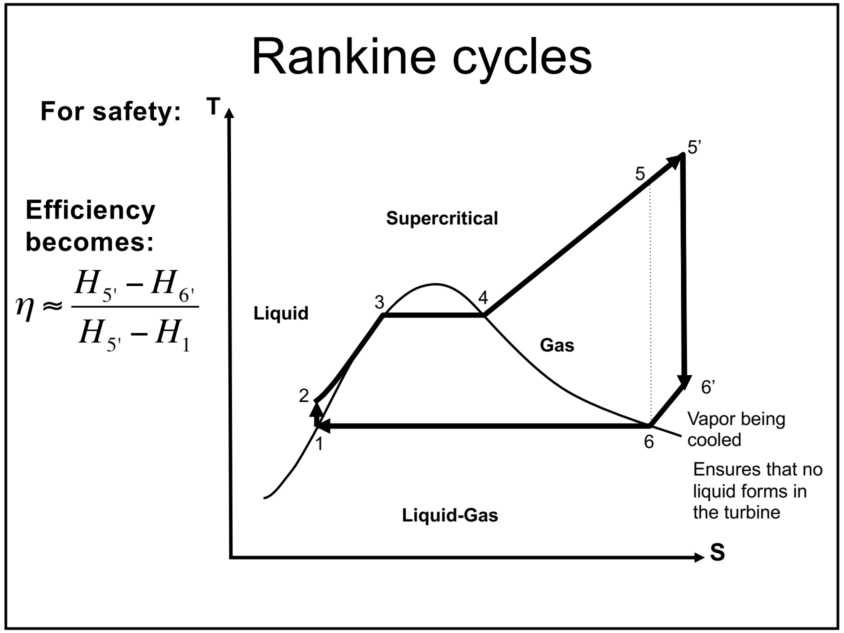
$$\longrightarrow \eta \approx \frac{H_5 - H_6}{H_5 - H_1}$$

The enthalpy change during expansion

The enthalpy change during heating

Rankine cycles





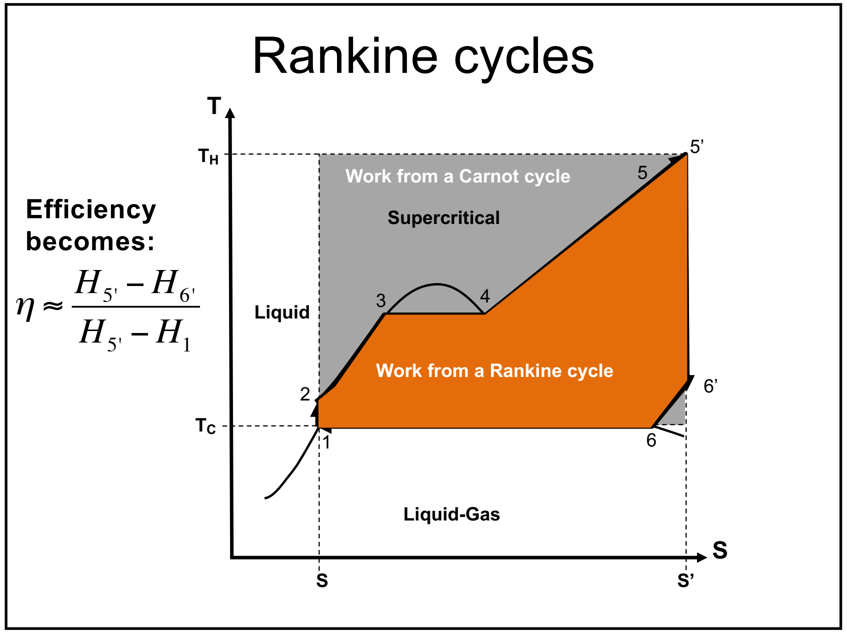
Rankine cycles

For safety:

Efficiency becomes:

$$\eta \approx \frac{H_{5'} - H_{6'}}{H_{5'} - H_{1}}$$

79



Rankine cycles

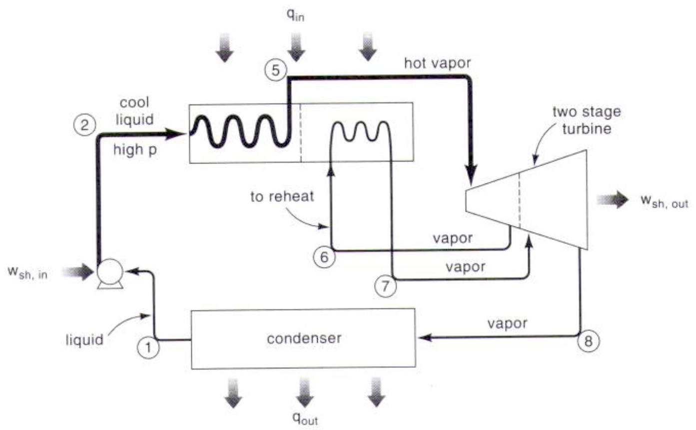
Efficiency becomes:

$$\eta \approx \frac{H_{5'} - H_{6'}}{H_{5'} - H_{1}}$$

80

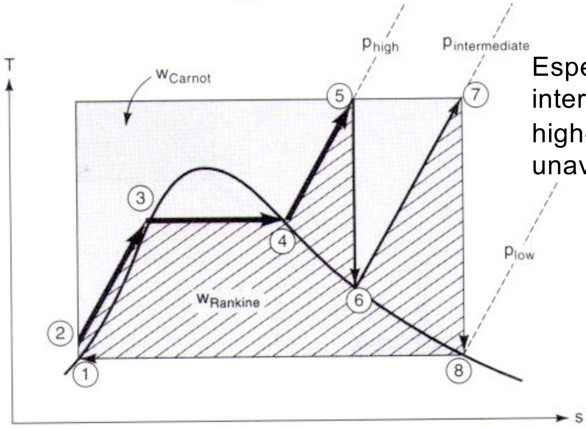
Rankine cycles

Approaching Carnot efficiency by reheating steam:



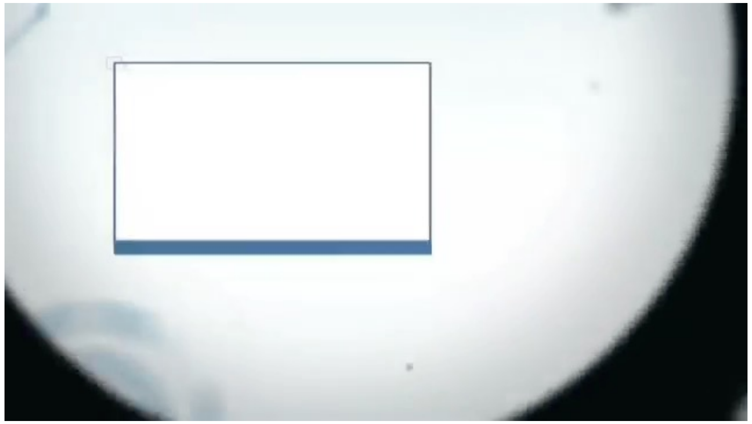
Rankine cycles

Approaching Carnot efficiency by reheating steam:



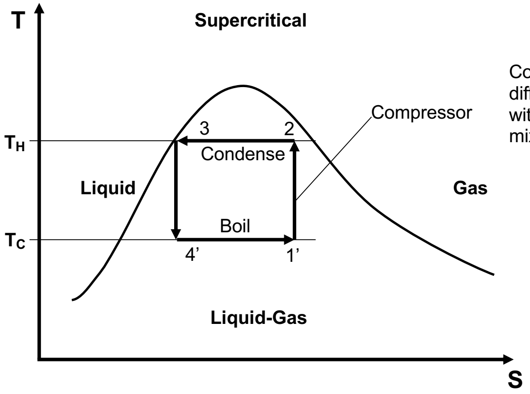
Especially interesting when high-T° source is unavailable!

Steam turbines



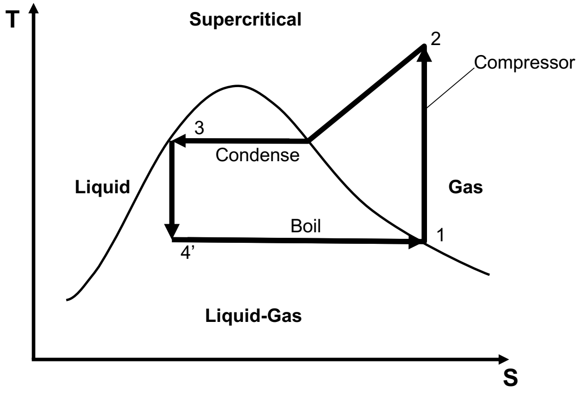
Problem 2
Let's try to calculate the Carnot efficiency of a gasoline engine by assuming that upon combustion all the higher heating value of the gas is used to heat the resulting product gases at constant volume.
Assume gasoline is pure octane (C_8H_{18}, Mw= 114), that air is 20% O_2 80% N_2 and that the amount of air needed is stoichiometric. You can assume that product gases are ideal gas and that their CV is 0.8 KJ/(kg K).

The Rankine refrigeration cycle

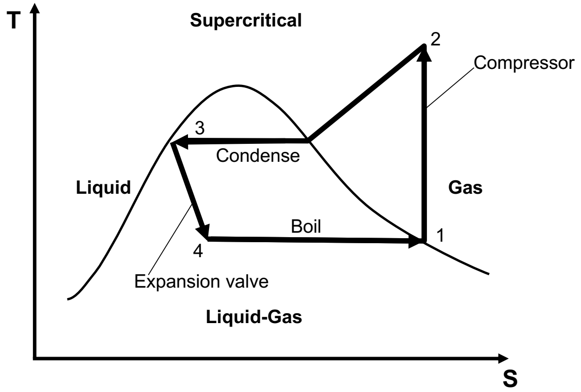


Compressors are difficult to run with a gas-liquid mixture!

The Rankine refrigeration cycle

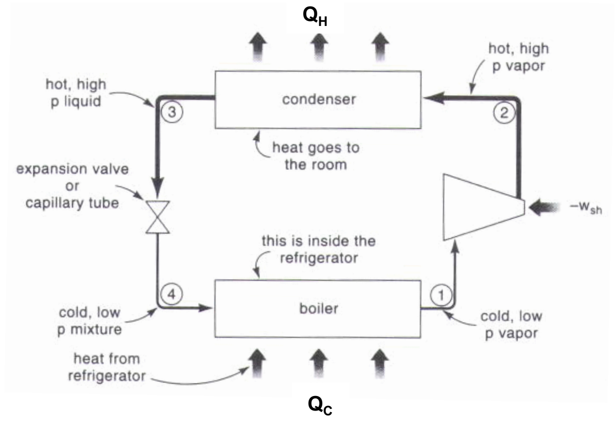


The Rankine refrigeration cycle

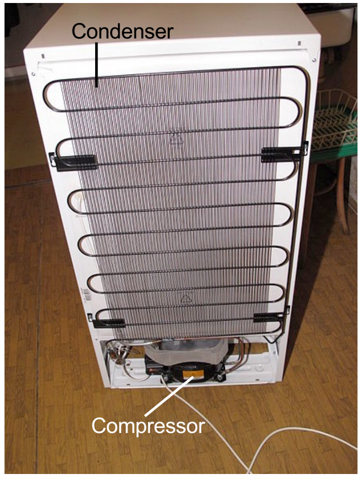


With an expansion valve the process is by definition irreversible and leads to a change in entropy!

The Rankine refrigeration cycle



The Rankine refrigeration cycle



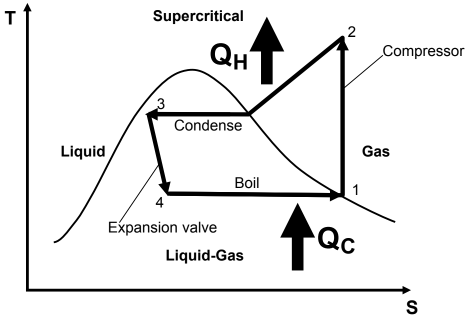
Expansion valve:

Source: Wikicommons media, http://www.xmtprp.com, http://www.fridgefilters.com/

The Rankine refrigeration cycle

$$COP_{\text{Refrigeration}} = \frac{Q_C}{W}$$

$$= \frac{H_1 - H_4}{H_2 - H_1}$$



$$COP_{\text{Heat pump}} = \frac{-Q_{\text{H}}}{W} = \frac{H_2 - H_3}{H_2 - H_1}$$

Problem 3
Let's calculate the efficiency of a typical refrigerator/freezer in your home. A typical refrigeration fluid is tetrafluoroethane (R134a). The evaporator usually runs at room temperature and R134a boils at -26°C. Even on hot summer days, which can reach on average 29°C in Switzerland, the refrigerator condenser fluid should always remain at least 10°C hotter than the environment.

Assume there is 1 kg of refrigerant. You can also assume that all the work given by the compressor is converted to enthalpy in the fluid. Finally, assume that the expansion valve is an isentropic process. Use the data in the annex.

What is the efficiency?

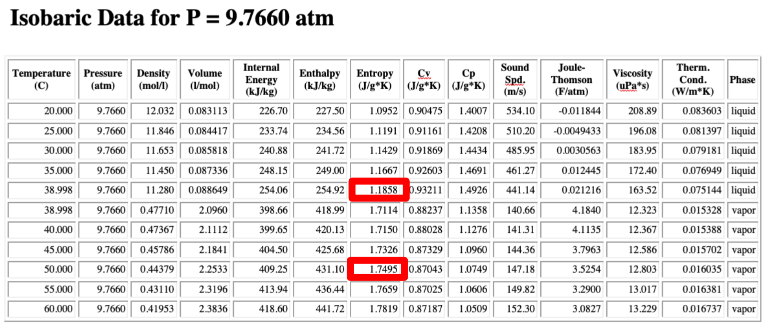
Assuming that a refrigerator uses about 500 Watt, what is its cooling power and how does that compare to a Carnot refrigerator?

Hint: look at figure 1.12. Find the data points on the graph at which we need to determine the properties. You can find out these properties by what you know about the Rankine cycle.

Vapor Phase Data

Data on Saturation Curve

Temperature (C)	Pressure (atm)	Density (mol/l)	Volume (l/mol)	Internal Energy (kJ/kg)	Enthalpy (kJ/kg)	Entropy (J/g*K)	Cv (J/g*K)	Cp (J/g*K)	Sound Spd. (m/s)	Joule-Thomson (F/atm)	Viscosity (uPa*s)	Therm. Cond. (W/m*K)	Phase
-31.000	0.79392	0.041473	24.112	360.68	379.69	1.7526	0.67550	0.77755	145.04	9.0236	9.5996	0.0089085	vapor
-26.000	1.0034	0.051698	19.343	363.55	382.82	1.7471	0.68859	0.79444	145.67	8.3821	9.7818	0.0093196	vapor
-21.000	1.2543	0.063820	15.669	366.42	385.94	1.7422	0.70194	0.81215	146.19	7.8137	9.9633	0.0097333	vapor
-16.000	1.5522	0.078086	12.806	369.28	389.02	1.7379	0.71555	0.83075	146.59	7.3070	10.144	0.010150	vapor
-11.000	1.9028	0.094762	10.553	372.12	392.06	1.7341	0.72941	0.85031	146.85	6.8534	10.325	0.010571	vapor
-6.0000	2.3121	0.11414	8.7612	374.95	395.06	1.7307	0.74354	0.87094	146.98	6.4458	10.507	0.010996	vapor
-1.0000	2.7865	0.13654	7.3241	377.75	398.02	1.7276	0.75792	0.89272	146.96	6.0788	10.689	0.011427	vapor
4.0000	3.3325	0.16231	6.1612	380.53	400.92	1.7250	0.77254	0.91581	146.79	5.7479	10.874	0.011865	vapor
9.0000	3.9569	0.19183	5.2128	383.27	403.76	1.7226	0.78742	0.94036	146.47	5.4491	11.061	0.012312	vapor
14.000	4.6670	0.22556	4.4334	385.98	406.53	1.7204	0.80254	0.96659	145.97	5.1794	11.252	0.012769	vapor
19.000	5.4699	0.26398	3.7882	388.64	409.22	1.7184	0.81792	0.99476	145.31	4.9360	11.448	0.013239	vapor
24.000	6.3734	0.30764	3.2506	391.25	411.82	1.7166	0.83357	1.0252	144.45	4.7166	11.651	0.013725	vapor
29.000	7.3852	0.35720	2.7996	393.80	414.33	1.7148	0.84951	1.0585	143.40	4.5193	11.863	0.014232	vapor
34.000	8.5135	0.41340	2.4190	396.27	416.72	1.7131	0.86577	1.0950	142.14	4.3422	12.086	0.014764	vapor
39.000	9.7666	0.47713	2.0958	398.66	418.99	1.7114	0.88238	1.1358	140.66	4.1839	12.323	0.015329	vapor
44.000	11.153	0.54948	1.8199	400.96	421.11	1.7096	0.89941	1.1818	138.95	4.0430	12.579	0.015935	vapor
49.000	12.683	0.63174	1.5829	403.13	423.07	1.7077	0.91692	1.2345	136.98	3.9184	12.858	0.016595	vapor



Isobaric Data for P = 9.7660 atm

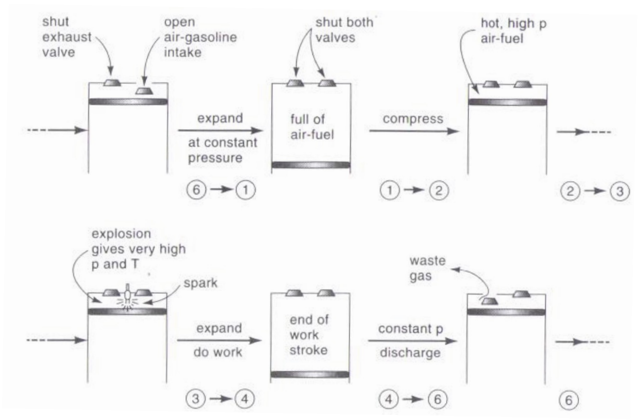
Temperature (C)	Pressure (atm)	Density (mol/l)	Volume (l/mol)	Internal Energy (kJ/kg)	Enthalpy (kJ/kg)	Entropy (J/g*K)	Cv (J/g*K)	Cp (J/g*K)	Sound Spd. (m/s)	Joule-Thomson (F/atm)	Viscosity (uPa*s)	Therm. Cond. (W/m*K)	Phase
20.000	9.7660	12.032	0.083113	226.70	227.50	1.0952	0.90475	1.4007	534.10	-0.011844	208.89	0.083603	liquid
25.000	9.7660	11.846	0.084417	233.74	234.56	1.1191	0.91161	1.4208	510.20	-0.0049433	196.08	0.081397	liquid
30.000	9.7660	11.653	0.085818	240.88	241.72	1.1429	0.91869	1.4434	485.95	0.0030563	183.95	0.079181	liquid
35.000	9.7660	11.450	0.087336	248.15	249.00	1.1667	0.92603	1.4691	461.27	0.012445	172.40	0.076949	liquid
38.998	9.7660	11.280	0.088649	254.06	254.92	1.1858	0.93211	1.4926	441.14	0.021216	163.52	0.075144	liquid
38.998	9.7660	0.47710	2.0960	398.66	418.99	1.7114	0.88237	1.1358	140.66	4.1840	12.323	0.015328	vapor
40.000	9.7660	0.47367	2.1112	399.65	420.13	1.7150	0.88028	1.1276	141.31	4.1135	12.367	0.015388	vapor
45.000	9.7660	0.45786	2.1841	404.50	425.68	1.7326	0.87329	1.0960	144.36	3.7963	12.586	0.015702	vapor
50.000	9.7660	0.44379	2.2533	409.25	431.10	1.7495	0.87043	1.0749	147.18	3.5254	12.803	0.016035	vapor
55.000	9.7660	0.43110	2.3196	413.94	436.44	1.7659	0.87025	1.0606	149.82	3.2900	13.017	0.016381	vapor
60.000	9.7660	0.41953	2.3836	418.60	441.72	1.7819	0.87187	1.0509	152.30	3.0827	13.229	0.016737	vapor

Outline of Part 1: Thermo

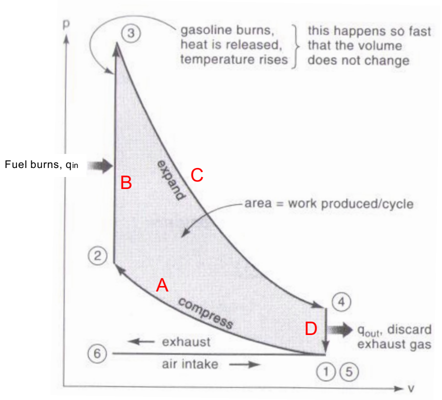
Objective: Derive and understand the physical laws that characterize and limit energy conversion systems

- 1st Law of Thermodynamics
  - Internal energy
  - Work
  - Enthalpy
- 2nd Law of Thermodynamics
  - Entropy
  - Reversible and irreversible processes
  - State functions
- Heat to work conversion
  - T-S diagrams
  - Idealized systems (Carnot cycle)
- Real heat to work and work to heat conversion systems
  - Rankine cycles
  - Refrigeration cycles and heat pumps
  - **Engines**
- Exergy: calculating the maximum work that can be produced/recovered
- Electrical systems
  - Electrical machines
  - Fuel cells

Gasoline engines: the Otto cycle



Gasoline engines: the Otto cycle



The cycle:

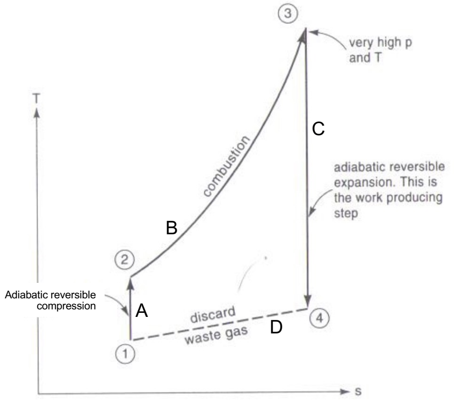
A. Adiabatic compression of the fuel mixture

B. Constant volume heating of the fuel during explosion

C. Adiabatic expansion of the hot gas (produces work)

D. Exhaust exits with residual heat at constant volume (removes heat)

Gasoline engines: the Otto cycle



The cycle:

A. Adiabatic compression

$$Q=0 \text{ and } \Delta \mathrm{U}_{1\rightarrow 2}=W_{in}=C_V(T_2-T_1)$$

B. Constant volume heating

$$W=0 \text{ and } \mathrm{Q}_{in}=C_V(T_3-T_2)$$

C. Adiabatic expansion

$$Q=0 \text{ and } \Delta \mathrm{U}_{3\rightarrow 4}=W_{out}=C_V(T_3-T_4)$$

D. Constant volume cooling

$$W=0 \text{ and } \mathrm{Q}_{out}=C_V(T_4-T_1)$$

$$\eta=\frac{W}{Q_{in}}=\frac{Q_{in}-Q_{out}}{Q_{in}}=\frac{C_V(T_3-T_2)-C_V(T_4-T_1)}{C_V(T_3-T_2)}$$

Gasoline engines: the Otto cycle

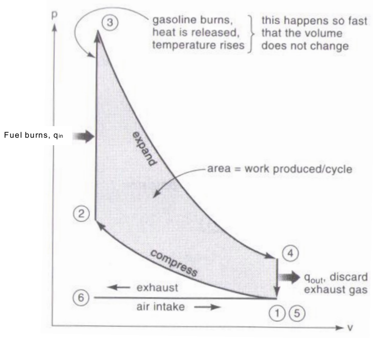
$$\eta=\frac{C_V(T_3-T_2)-C_V(T_4-T_1)}{C_V(T_3-T_2)}$$

$$=\frac{(T_3-T_2)-(T_4-T_1)}{(T_3-T_2)}$$

For adiabatic changes we can write:

$$\frac{T_2}{T_1}=\left(\frac{V_1}{V_2}\right)^{k-1} \quad \left(\frac{V_4}{V_3}\right)^{k-1}=\frac{T_3}{T_4}$$

Notice that V_1=V_4 and V_2=V_3.



$$\eta=\frac{(1-T_2/T_3)-(T_4/T_3-T_1/T_3)}{(1-T_2/T_3)}=\frac{(1-T_2/T_3)-(T_1/T_2-T_1/T_3)}{(1-T_2/T_3)}=1-\frac{(T_1/T_2-T_1/T_3)}{(1-T_2/T_3)}=1-T_1/T_2\frac{(1-T_2/T_3)}{(1-T_2/T_3)}=1-T_1/T_2$$

$$\eta=1-\frac{T_1}{T_2}=1-\left(\frac{V_2}{V_1}\right)^{1-k}=1-r_c^{1-k}$$

Gasoline engines: the Otto cycle

$$\eta = 1 - \left(\frac{V_2}{V_1}\right)^{1-k} = 1 - r_c^{1-k}$$

The compression ratio:

$$r_c = \frac{V_1}{V_2} = \frac{V_4}{V_3}$$

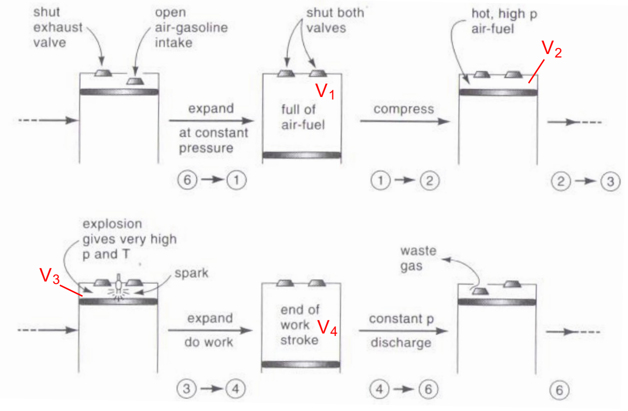
In gasoline engines:

$r_c \approx 8\text{-}9$

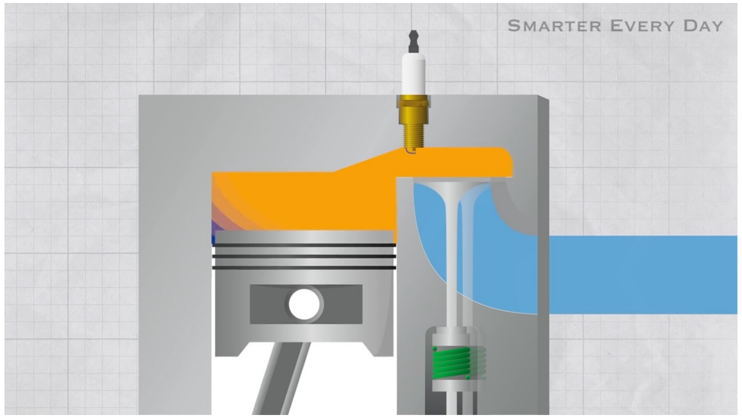
$\eta \approx 45\%$

In a real engine:

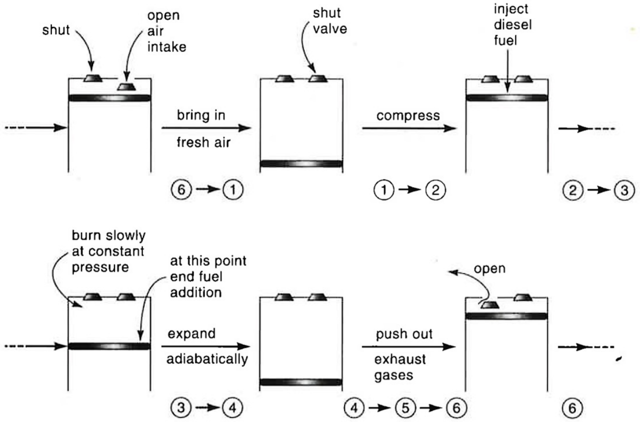
$\eta \approx 20\text{-}35\%$



Gasoline engines

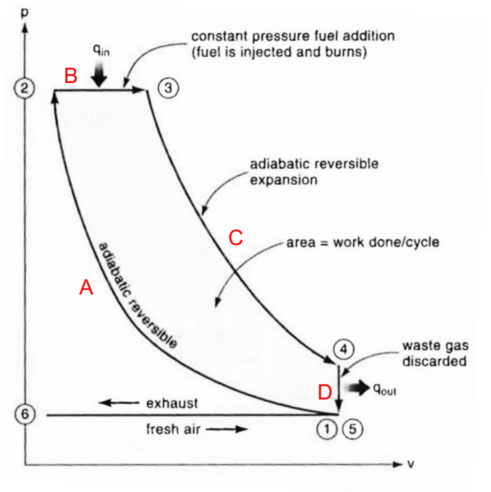


Diesel engines: the Diesel cycle



101

Diesel engines: the Diesel cycle



The cycle:

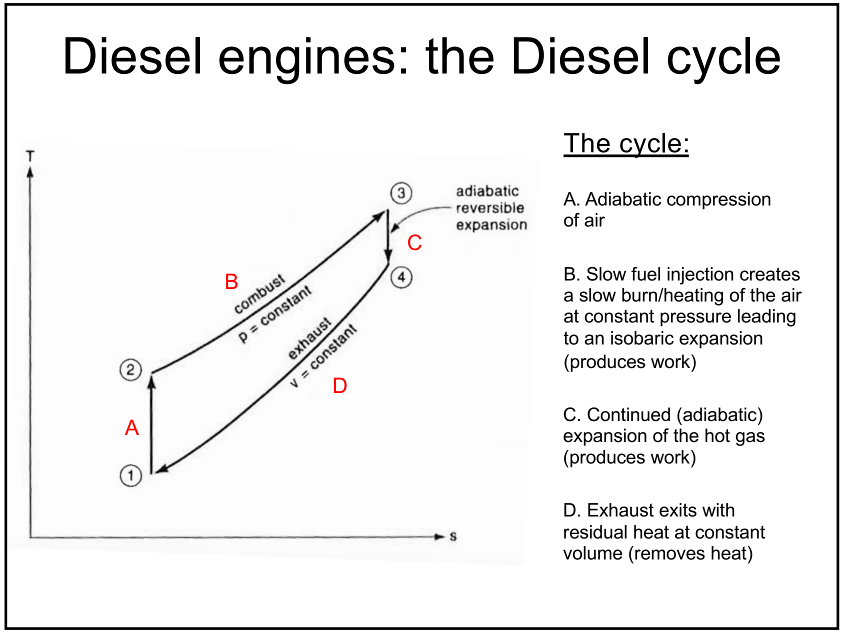
A. Adiabatic compression of air

B. Slow fuel injection creates a slow burn/heating of the air at constant pressure leading to an isobaric expansion (produces work)

C. Continued (adiabatic) expansion of the hot gas (produces work)

D. Exhaust exits with residual heat at constant volume (removes heat)

102



Diesel engines: the Diesel cycle

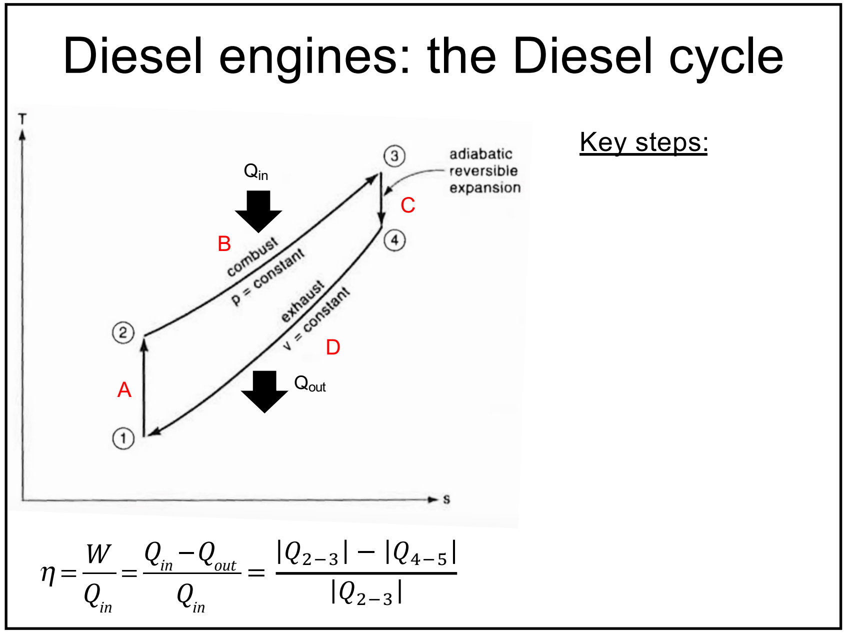
The cycle:

A. Adiabatic compression of air

B. Slow fuel injection creates a slow burn/heating of the air at constant pressure leading to an isobaric expansion (produces work)

C. Continued (adiabatic) expansion of the hot gas (produces work)

D. Exhaust exits with residual heat at constant volume (removes heat)

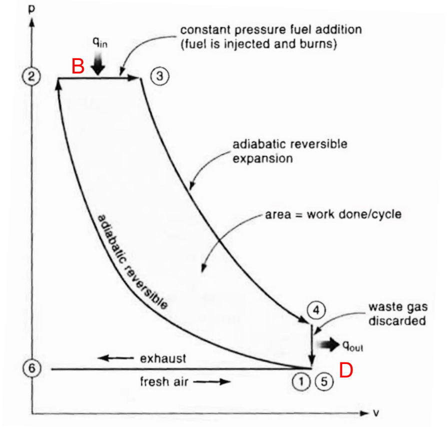


Diesel engines: the Diesel cycle

Key steps:

$$\eta = \frac{W}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = \frac{|Q_{2-3}| - |Q_{4-5}|}{|Q_{2-3}|}$$

Diesel engines: the Diesel cycle



Key steps:

B. Constant pressure heating

$$Q_{in} = \Delta U + P\Delta V = \Delta H = C_P(T_3 - T_2)$$

D. Constant volume cooling

$$W = 0 \text{ and } Q_{out} = C_V(T_4 - T_1)$$

$$\eta = \frac{W}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = \frac{|Q_{2-3}| - |Q_{4-5}|}{|Q_{2-3}|} = \frac{C_P(T_3 - T_2) - C_V(T_4 - T_1)}{C_P(T_3 - T_2)}$$

Diesel engines: the Diesel cycle

$$\eta = \frac{W}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = \frac{C_P(T_3 - T_2) - C_V(T_4 - T_1)}{C_P(T_3 - T_2)}$$

$$= 1 - \frac{C_V}{C_P}\frac{(T_4 - T_1)}{(T_3 - T_2)} = 1 - \frac{1}{k}\frac{(T_4 - T_1)}{(T_3 - T_2)}$$

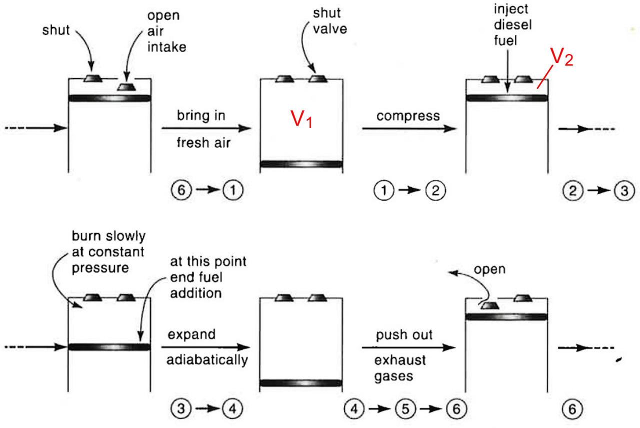
We can define:

The compression ratio:

$$r_c = \frac{V_1}{V_2}$$

Same as for gasoline engines…

Diesel engines: the Diesel cycle



Diesel engines: the Diesel cycle

$$\eta = \frac{W}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = \frac{C_P(T_3 - T_2) - C_V(T_4 - T_1)}{C_P(T_3 - T_2)}$$

$$= 1 - \frac{C_V}{C_P}\frac{(T_4 - T_1)}{(T_3 - T_2)} = 1 - \frac{1}{k}\frac{(T_4 - T_1)}{(T_3 - T_2)}$$

We can define:

The compression ratio:

$$r_c = \frac{V_1}{V_2}$$

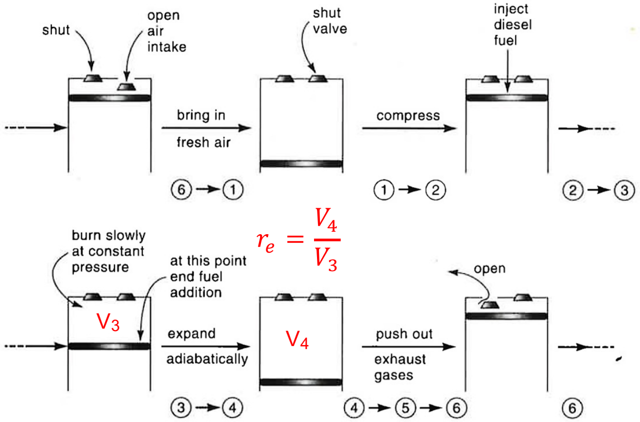
Same as for gasoline engines…

The expansion ratio:

$$r_e = \frac{V_4}{V_3}$$

Defines the further expansion after the injection of fuel

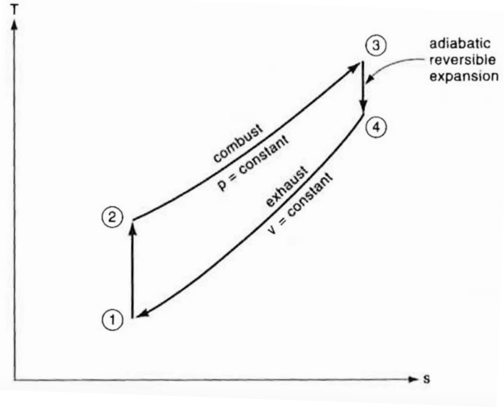
Diesel engines: the Diesel cycle



$$r_e = \frac{V_4}{V_3}$$

Diesel engines: the Diesel cycle

Steps 1-2 and 3-4 are adiabatic…



The compression ratio:

$$r_c = \frac{V_1}{V_2} = \left(\frac{T_2}{T_1}\right)^{1/(k-1)}$$

$$T_2 = T_1 (r_c)^{k-1}$$

$$\rightarrow T_1 = T_2 \left(\frac{1}{r_c}\right)^{k-1}$$

The expansion ratio:

$$r_e = \frac{V_4}{V_3} = \left(\frac{T_3}{T_4}\right)^{1/(k-1)}$$

$$T_3 = T_4 (r_e)^{k-1}$$

$$\rightarrow T_4 = T_3 \left(\frac{1}{r_e}\right)^{k-1}$$

Diesel engines: the Diesel cycle

$$\eta = 1 - \frac{1}{k}\frac{(T_4 - T_1)}{(T_3 - T_2)} \qquad T_1 = T_2\left(\frac{1}{r_c}\right)^{k-1} \qquad T_4 = T_3\left(\frac{1}{r_e}\right)^{k-1}$$

Let’s further define:

$$\frac{(T_4 - T_1)}{(T_3 - T_2)} = \frac{T_3\left(\frac{1}{r_e}\right)^{k-1} - T_2\left(\frac{1}{r_c}\right)^{k-1}}{(T_3 - T_2)} = \frac{\frac{T_3(T_3 - T_2)}{T_3 - T_2}\left(\frac{1}{r_e}\right)^{k-1} - \frac{T_2(T_3 - T_2)}{T_3 - T_2}\left(\frac{1}{r_c}\right)^{k-1}}{(T_3 - T_2)}$$

$$= \frac{\frac{(T_3 - T_2)}{1 - \frac{T_2}{T_3}}\left(\frac{1}{r_e}\right)^{k-1} - \frac{(T_3 - T_2)}{\frac{T_3}{T_2} - 1}\left(\frac{1}{r_c}\right)^{k-1}}{(T_3 - T_2)} = \frac{(T_3 - T_2)\left(\frac{\left(\frac{1}{r_e}\right)^{k-1}}{1 - T_2/T_3} - \frac{\left(\frac{1}{r_c}\right)^{k-1}}{T_3/T_2 - 1}\right)}{(T_3 - T_2)}$$

$$= \left(\frac{\left(\frac{1}{r_e}\right)^{k-1}}{1 - T_2/T_3} - \frac{\left(\frac{1}{r_c}\right)^{k-1}}{T_3/T_2 - 1}\right)$$

Diesel engines: the Diesel cycle

$$\eta = 1 - \frac{1}{k}\left(\frac{\left(\frac{1}{r_e}\right)^{k-1}}{1 - T_2/T_3} - \frac{\left(\frac{1}{r_c}\right)^{k-1}}{T_3/T_2 - 1}\right)$$

Step 2→3 is isobaric

$$P_2 = P_3$$

Step 4→1 is isochoric

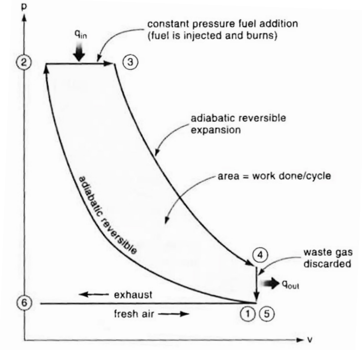
$$V_4 = V_1$$

With the ideal gas law:

$$\frac{T_3}{T_2} = \frac{P_3 V_3}{P_2 V_2}$$

$$= \frac{V_3}{V_2} = \frac{V_3/V_4}{V_2/V_1} = \frac{r_c}{r_e}$$

$$\eta = 1 - \frac{1}{k}\left(\frac{\left(\frac{1}{r_e}\right)^{k-1}}{1 - r_e/r_C} - \frac{\left(\frac{1}{r_c}\right)^{k-1}}{r_C/r_e - 1}\right)$$



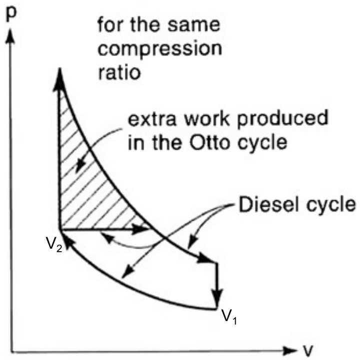
Diesel engines: the Diesel cycle

$$\eta = 1 - \frac{1}{k}\left(\frac{\left(\frac{1}{r_e}\right)^{k-1}}{1 - r_e/r_C} - \frac{\left(\frac{1}{r_c}\right)^{k-1}}{r_C/r_e - 1}\right)$$

$$= 1 - \frac{1}{k}\left(\frac{\left(\frac{1}{r_e}\right)^{k}}{1/r_e - 1/r_C} - \frac{\left(\frac{1}{r_c}\right)^{k}}{1/r_e - 1/r_C}\right)$$

$$= 1 - \frac{1}{k}\frac{\left(\frac{1}{r_e}\right)^{k} - \left(\frac{1}{r_c}\right)^{k}}{1/r_e - 1/r_C}$$

For the same compression ratio, $r_c = \frac{V_1}{V_2}$ the Otto cycle is more efficient.



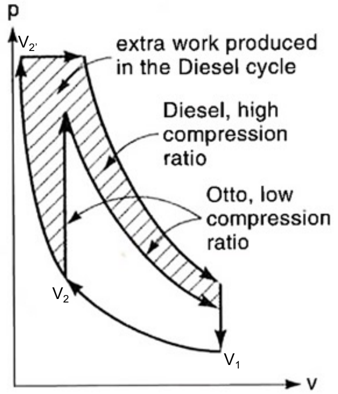
Diesel engines: the Diesel cycle

$$\eta = 1 - \frac{1}{k}\left(\frac{\left(\frac{1}{r_e}\right)^{k-1}}{1 - r_e/r_C} - \frac{\left(\frac{1}{r_c}\right)^{k-1}}{r_C/r_e - 1}\right)$$

$$= 1 - \frac{1}{k}\left(\frac{\left(\frac{1}{r_e}\right)^{k}}{1/r_e - 1/r_C} - \frac{\left(\frac{1}{r_c}\right)^{k}}{1/r_e - 1/r_C}\right)$$

$$= 1 - \frac{1}{k}\frac{\left(\frac{1}{r_e}\right)^{k} - \left(\frac{1}{r_c}\right)^{k}}{1/r_e - 1/r_C}$$

But in practice, higher compression ratios can be achieved (20 vs. 8-9 for gasoline engines → This is because only air is compressed instead of a gasoline fuel mixture.

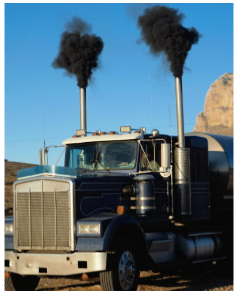


Diesel engines: the Diesel cycle

The higher compression ratios, lead to theoretical efficiencies close to 60%.

In real engines, efficiencies can reach a little over 40%, making them more fuel efficient than gasoline engines.

Lack of pre-mixing causes gradients with uneven combustion:



Higher compression = higher temperature = higher NOx formation

ChE-304 Problem Set 3

Week 3

Problem 1

A change in entropy for an ideal gas system undergoing a change in entropy where both, T, V and P can be calculated with:

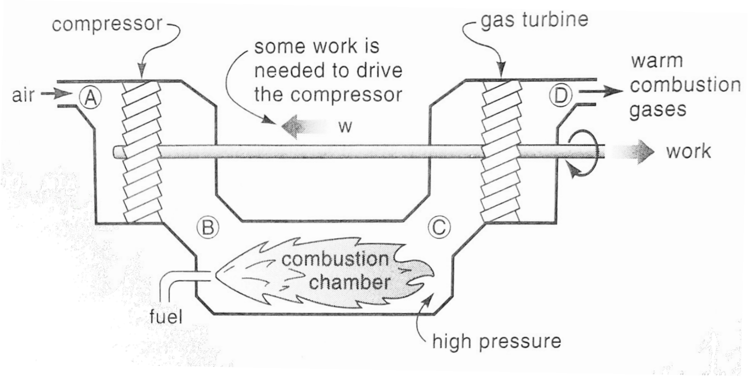
$$\Delta S = n\left(C_p \ln\left(\frac{T_2}{T_1}\right) - R\ln\left(\frac{P_2}{P_1}\right)\right)$$

or

$$\Delta S = n\left(C_V \ln\left(\frac{T_2}{T_1}\right) + R\ln\left(\frac{V_2}{V_1}\right)\right)$$

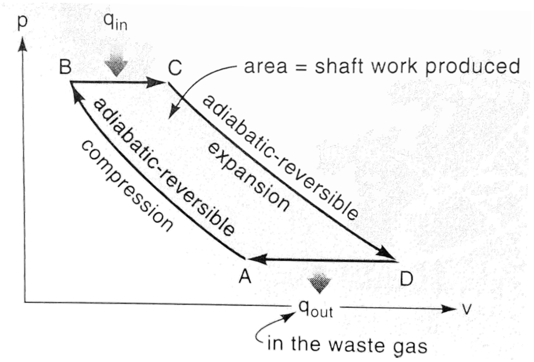
Prove that these expressions hold for a single change where both T, V and P are changing starting from the definition of ΔS: $\Delta S = \int \frac{dQ_{rev}}{T}$

Gas turbines and jet engines: the Brayton cycle



Advantage over the Rankine cycle: no need for a heat exchange network.

Gas turbines and jet engines: the Brayton cycle



The cycle:

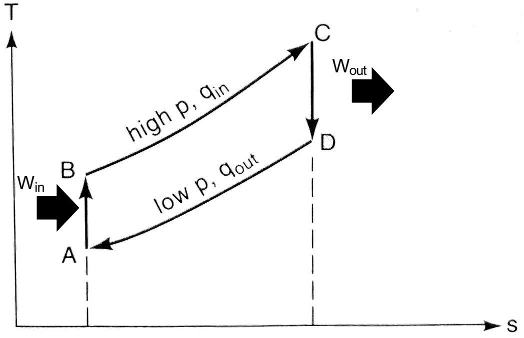
A-B. Air enters the turbine and is compressed adiabatically.

B-C. Compressed air is mixed with burning fuel: heating occurs at constant pressure and volume expands

C-D. Hot gas is expanded back to atmospheric pressure adiabatically and produces work

D-A. Exhaust exits and cools back down at constant pressure (and contracts in doing so).

Gas turbines and jet engines: the Brayton cycle



The cycle:

A-B. Air enters the turbine and is compressed adiabatically.

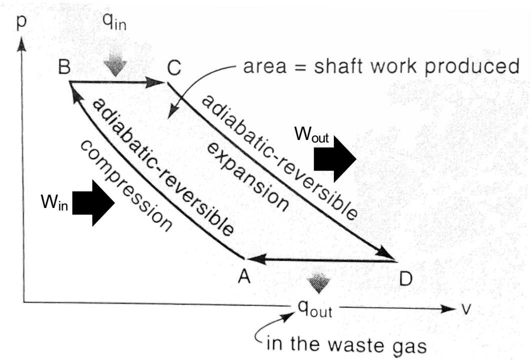
B-C. Compressed air is mixed with burning fuel: heating occurs at constant pressure and volume expands

C-D. Hot gas is expanded back to atmospheric pressure adiabatically and produces work

D-A. Exhaust exits and cools back down at constant pressure (and contracts in doing so).

$$\eta = \frac{Excess\ work}{Heat\ released\ by\ the\ fuel} = \frac{|W_{CD}| - |W_{AB}|}{|Q_{BC}|}$$

Gas turbines and jet engines: the Brayton cycle



Key steps:

B-C. Constant pressure heating:

$$\begin{aligned} Q &= \Delta U + P\Delta V \\ &= \Delta H \\ &= C_P(T_C - T_B) \end{aligned}$$

D-A. Constant pressure cooling:

$$\begin{aligned} Q &= \Delta U + P\Delta V \\ &= \Delta H \\ &= C_P(T_D - T_A) \end{aligned}$$

By energy balance:

$$\eta = \frac{|W_{CD}| - |W_{AB}|}{|Q_{BC}|} = \frac{|Q_{BC}| - |Q_{AD}|}{|Q_{BC}|} = \frac{C_p(T_C - T_B) - C_p(T_D - T_A)}{C_p(T_C - T_B)}$$

Gas turbines and jet engines: the Brayton cycle

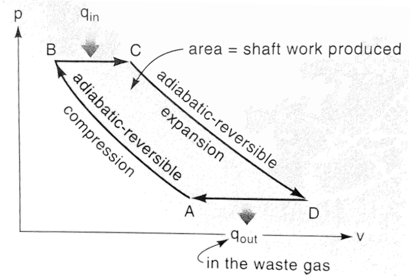
$$\eta = \frac{(T_C - T_B) - (T_D - T_A)}{(T_C - T_B)}$$

Since A-B and C-B are adiabatic:

$$\left(\frac{T_B}{T_A}\right) = \left(\frac{P_B}{P_A}\right)^{\frac{k-1}{k}} \qquad \left(\frac{T_C}{T_D}\right) = \left(\frac{P_C}{P_D}\right)^{\frac{k-1}{k}}$$

And $P_B = P_C$ $\qquad P_A = P_D$

$$\left(\frac{T_B}{T_A}\right) = \left(\frac{P_B}{P_A}\right)^{\frac{k-1}{k}} = \left(\frac{P_C}{P_D}\right)^{\frac{k-1}{k}} = \left(\frac{T_C}{T_D}\right)$$



$$\eta = 1 - \frac{(T_D - T_A)}{(T_C - T_B)} = 1 - \frac{T_A}{T_B}\frac{\left(\frac{T_D}{T_A} - 1\right)}{\left(\frac{T_C}{T_B} - 1\right)} = 1 - \frac{T_A}{T_B}\frac{\left(\frac{T_C}{T_B} - 1\right)}{\left(\frac{T_C}{T_B} - 1\right)} = 1 - \frac{T_A}{T_B} = 1 - \left(\frac{P_A}{P_B}\right)^{\frac{k-1}{k}}$$

Gas turbines and jet engines: the Brayton cycle

$$\eta = 1 - \left(\frac{P_A}{P_B}\right)^{\frac{k-1}{k}}$$ ➡ This means that the higher the compression, the higher the efficiency.

Higher compression ratios also leads to higher post combustion temperatures, which is limited by materials (material limits are between 1200-1500°C).

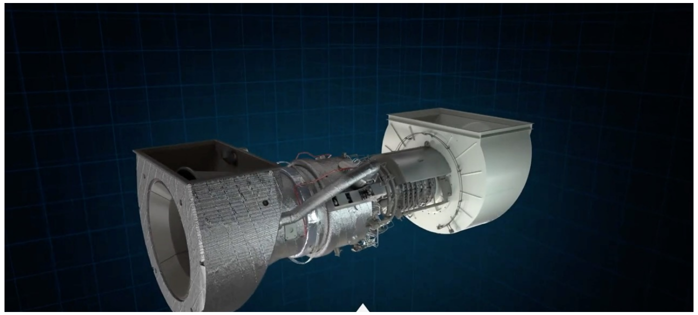
Practical limits of a gas turbine lead to pressure ratios around 20 and theoretical efficiencies around 55-60%.

The compressor employs a significant amount of work (about 80% of the output work* is employed by the compressor). And compressors are never more than 80% efficient.

Real world efficiencies can now reach about 40-45%.

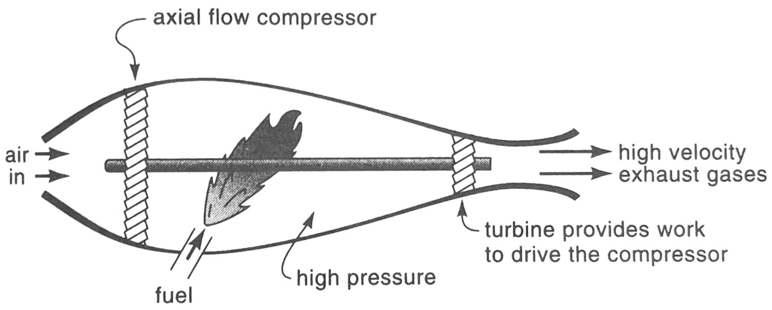
*which is not the net work, but the work done by the output turbine…

A gas turbine



https://www.youtube.com/watch?v=jrWHi77oAWI

Brayton cycles applied to jet engines



For a jet engine: same general idea but a different geometry that is built to accelerate the exiting gas.

Aircraft evolution

Boeing 747-100 (1966)

Boeing 777X (2019)

Brayton cycles applied to jet engines

Ultimately, for a jet engine we care about *propulsive power* and the amount produced with respect to the thermal energy of the fluid.

$$\eta_{overall} = \frac{propulsive\ power}{\dot{Q}_{in}}$$

It is useful to break this efficiency down into two parts:

$$\eta_{overall} = \eta_{thermal}\eta_{propulsive}$$

$\eta_{thermal}$ Represents the ratio of kinetic energy created over the thermal energy given by the fuel.

If we neglect the mass of fuel added to the air: $\dot{m}_{air,in} = \dot{m}_{air,out} = \dot{m}_{air}$

$$\eta_{thermal} = \frac{(m_{air,out} v_{out}^2 - m_{air,in} v_{in}^2)/2}{Q_{in}} = 1 - \frac{T_A}{T_B}$$

Because all of the pV work is used to accelerate the gas.

Brayton cycles applied to jet engines

Ultimately, for a jet engine we care about *propulsive power* and the amount produced with respect to the thermal energy of the fluid.

$$\eta_{overall} = \frac{propulsive\ power}{\dot{Q}_{in}}$$

It is useful to break this efficiency down into two parts:

$$\eta_{overall} = \eta_{thermal}\eta_{propulsive}$$

$\eta_{propulsive}$ The ratio of propulsive power produced, divided by the rate of production of the kinetic energy transferred to the gas.

$$\eta_{propulsive} = \frac{propulsive\ power}{rate\ of\ production\ of\ propulsive\ kinetic\ energy}$$

Brayton cycles applied to jet engines

$$\eta_{propulsive} = \frac{propulsive\ power}{rate\ of\ production\ of\ propulsive\ kinetic\ energy}$$

Again, neglecting the mass of fuel, we can just use the mass of air:

$$\eta_{propulsive} = \frac{propulsive\ power}{\dot{m}_{air}\left(v_{out}^2 - v_{in}^2\right)/2}$$

Flight speed, which is equivalent to the speed incoming air v_{in}

$$propulsive\ power = v_{flight} \times Thrust$$

$$= v_{in}\left(\dot{m}_{air}(v_{out} - v_{in})\right)$$

$$\eta_{propulsive} = \frac{v_{in}\left(\dot{m}_{air}(v_{out} - v_{in})\right)}{\dot{m}_{air}\left(v_{out}^2 - v_{in}^2\right)/2} = \frac{2\,v_{in}(v_{out} - v_{in})}{(v_{out}+v_{in})(v_{out} - v_{in})} = \frac{2\,v_{in}}{v_{out} + v_{in}} = \frac{2}{1 + \frac{v_{out}}{v_{in}}}$$

Brayton cycles applied to jet engines

$$\eta_{propulsive} = \frac{2}{1 + \frac{v_{out}}{v_{in}}}$$

The propulsive efficiency only depends on speed and is the highest when the increase in speed is small.

But the airplane must maintain a high degree of thrust to:

- Counter air resistance (which is ignored in ideal calculations)
- Maintain the ability to accelerate

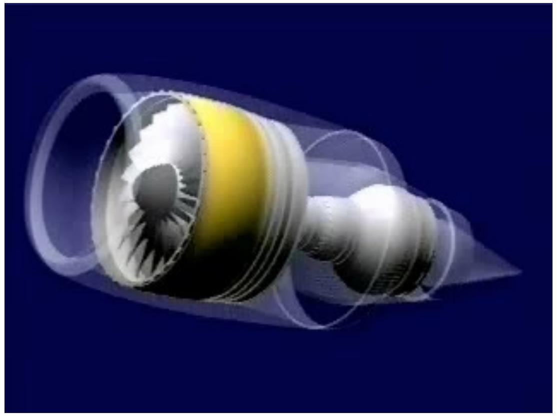
$thrust = \dot{m}_{air}(v_{out} - v_{in})$ Thrust decreases when air speed difference decreases.

The opposite of efficiency!

However, *thrust* increases with $\dot{m}_{air}$ while efficiency is unaffected.

→ The solution was to increase airflow while keeping speed differences small using so-called high bypass engines

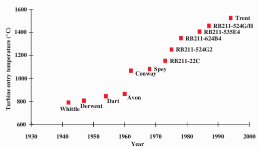
Modern engines are high bypass engines



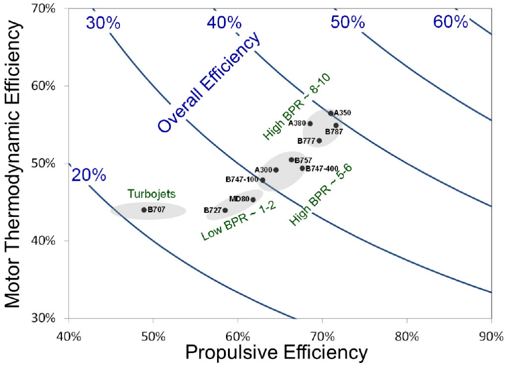
Source: USAF academy

Modern engines are high bypass engines

Recent advances have allowed major improvements in both thermodynamic and propulsive efficiency:



Through increases in T°



Through the development of high bypass engines

Outline of Part 1: Thermo

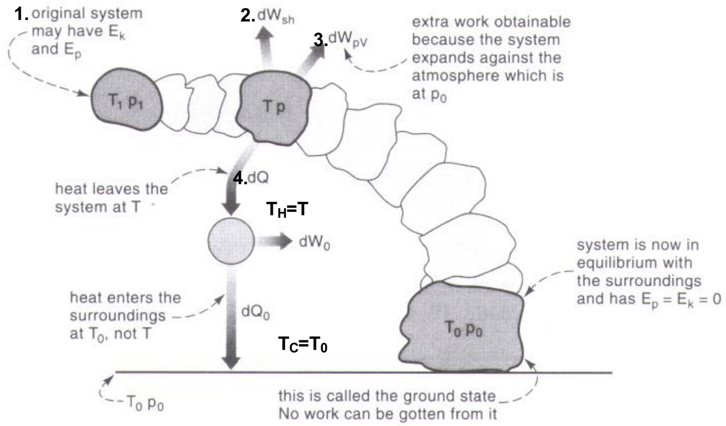
Objective: Derive and understand the physical laws that characterize and limit energy conversion systems

- 1st Law of Thermodynamics
  - Internal energy
  - Work
  - Enthalpy
- 2nd Law of Thermodynamics
  - Entropy
  - Reversible and irreversible processes
  - State functions
- Heat to work conversion
  - T-S diagrams
  - Idealized systems (Carnot cycle)
- Real heat to work and work to heat conversion systems
  - Rankine cycles
  - Refrigeration cycles and heat pumps
  - Engines
- **Exergy: calculating the maximum work that can be produced/recovered**
- Electrical systems
  - Electrical machines
  - Fuel cells

Exergy

Exergy (W_{ex}): the maximum amount of **useful** work obtainable for a given process.

Let's start with the ground state: All energy has to be accounted for as we bring our system to the ground state. This includes:



Is this just a Carnot Cycle? **No! E_p, E_k and dW_{sh} are included as well.**

Calculating ground state Exergy

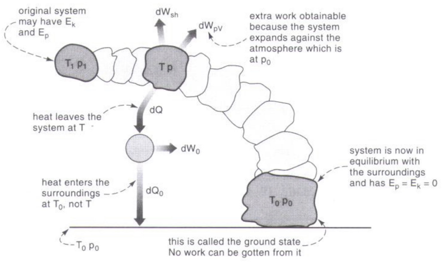
1st Law:

$$dE = dQ_0 - dW$$

Includes dU, dE_p and dE_k

Is the heat released to ground state

Includes all $dW = dW_{sh} + dW_{pV} + dW_0$



We know that the heat released by a Carnot engine is reversible and is at T_0:

$$dQ_0 = T_0 dS$$

$$dE = T_0 dS - dW_{sh} - dW_{pV} - dW_0 = T_0 dS - dW_{sh} - p_0 dV - dW_0$$

$$dW_{Ex} = dW_{sh} + dW_0 \quad = -dE + T_0 dS - p_0 dV$$

We integrate (with $E_0 = U_0$) :

$$W_{Ex,1\rightarrow 0} = -(U_0 - E_1) + T_0(S_0 - S_1) - p_0(V_0 - V_1)$$

Problem 2

A community (average T=27°C) has an enormous underground reservoir of high-pressure (inert) gas. The reservoir has the following properties:

T= 237 °C
P = 9.95 atm
V= 10^6 m^3
Depth = 2000 m below the surface
Cp = 36 J/(mol K)
Mw= 0.03 kg/mol

Assume that the gas is ideal.

What is the maximum amount of work that the community could extract out of the gas?

Outline of Part 1: Thermo

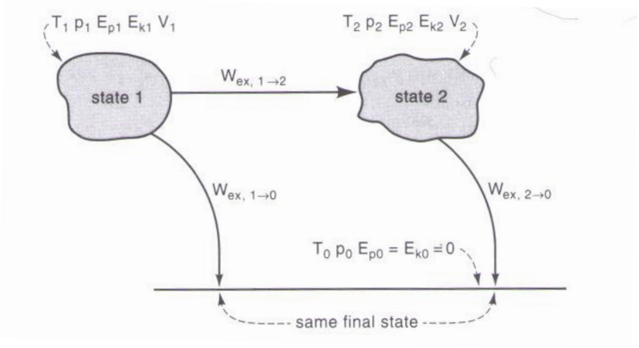
Objective: Derive and understand the physical laws that characterize and limit energy conversion systems

- 1st Law of Thermodynamics
  - Internal energy
  - Work
  - Enthalpy
- 2nd Law of Thermodynamics
  - Entropy
  - Reversible and irreversible processes
  - State functions
- Heat to work conversion
  - T-S diagrams
  - Idealized systems (Carnot cycle)
- Real heat to work and work to heat conversion systems
  - Rankine cycles
  - Refrigeration cycles and heat pumps
  - Engines
- **Exergy: calculating the maximum work that can be produced/recovered**
- Electrical systems
  - Electrical machines
  - Fuel cells

Exergy

Exergy (W_{ex}): the maximum amount of **useful** work obtainable for a given process (= a system going from state 1 to state 2).

For the calculation, we need: State 1, State 2 and the environment (State 0)



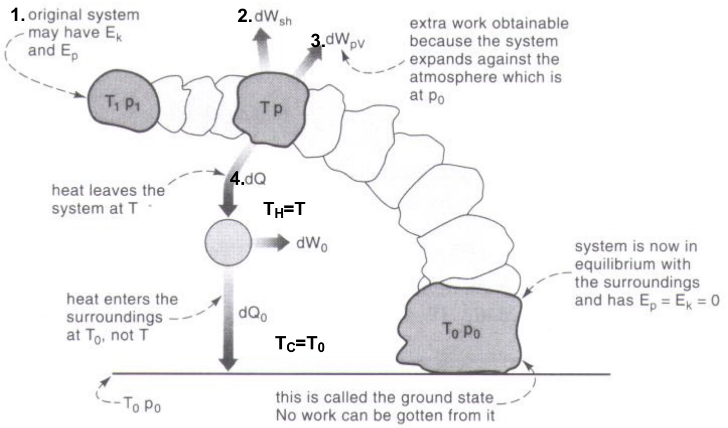
The exergy of this change is equal to the difference of the exergies of each state:

$$W_{ex,1\to2} = W_{ex,2\to0} - W_{ex,1\to0}$$

137

Calculating ground state Exergy

All energy has to be accounted for as we bring our system to the ground state. This includes:



Is this just a Carnot Cycle? **No! E_p, E_k and dW_{sh} are included as well.**

138

Calculating ground state Exergy

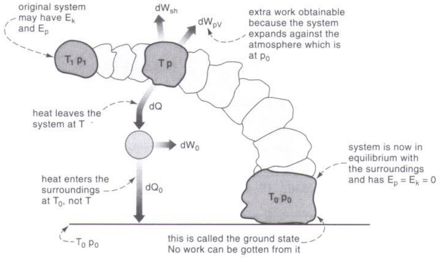
1st Law:

$$dE = dQ_0 - dW$$

Includes dU, dE_p and dE_k

Is the heat released to ground state

Includes all $dW = dW_{sh} + dW_{pV} + dW_0$



We know that the heat released by a Carnot engine is reversible and is at T_0:

$$dQ_0 = T_0 dS$$

$$dE = T_0 dS - dW_{sh} - dW_{pV} - dW_0 = T_0 dS - dW_{sh} - p_0 dV - dW_0$$

$$dW_{Ex} = dW_{sh} + dW_0 \quad = -dE + T_0 dS - p_0 dV$$

Calculating ground state Exergy

$$dW_{Ex} = -dE + T_0 dS - p_0 dV$$

We integrate (with $E_0 = U_0$) :

$$W_{Ex,1\to 0} = -(U_0 - E_1) + T_0(S_0 - S_1) - p_0(V_0 - V_1)$$

Assuming no changes in potential or kinetic energy:

$$W_{Ex,1\to 0} = -(U_0 - U_1) + T_0(S_0 - S_1) - p_0(V_0 - V_1)$$

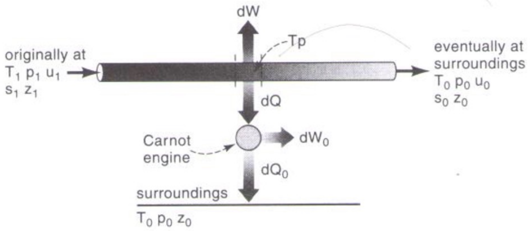
For a fuel that starts out at T_0 and P_0 (and *G=U-TS+PV*):

$$W_{Ex,1\to 0} = -\Delta G_0$$

For a change from State 1 to State 2:

$$W_{Ex,1\to 2} = W_{Ex,1\to 0} - W_{Ex,2\to 0} = -(E_2 - E_1) + T_0(S_2 - S_1) - p_0(V_2 - V_1)$$

Exergy in steady-state/flow systems



Starting with:

$$W_{Ex,1\to 0} = -(U_0 - U_1) + T_0(S_0 - S_1) - (p_0V_0 - p_1V_1)$$

By using enthalpy:

$$W_{Ex,1\to 0} = -(H_0 - \left[H_1 + E_p + E_k\right]) + T_0(S_0 - S_1)$$

Assuming that there is no change in kinetic and potential energy:

$$W_{Ex,1\to 2} = -(H_2 - H_1) + T_0(S_2 - S_1) = -\Delta G_0$$

Work lost in a real process

1st law for a change from State 1 to State 2:

$$\Delta E_{1\to 2,ideal} = T_0\Delta S - W_{sh,ideal} - p_0(V_2 - V_1) = T_0\Delta S - W_{Ex,1\to 2} - p_0(V_2 - V_1)$$

E is a state function! → the path does not matter.

$$\Delta E_{1\to 2,ideal} = \Delta E_{1\to 2,actual} = T_0\Delta S_{surr.} - W_{sh,actual} - p_0(V_2 - V_1)$$

Setting these two equations equal, we have:

$$W_{sh,lost} = W_{Ex,1\to 2} - W_{sh,actual} = T_0(S_2 - S_1) + T_0\Delta S_{surr.} = T_0(\Delta S_{sys.} + \Delta S_{surr.})$$
$$= T_0\Delta S_{tot.}$$

Important points:

$\Delta S_{tot.} = 0$ for an ideal change (no lost work).

$\Delta S_{sys.}$ is independent of whether or not the change is ideal (S is a state function).

The ideality of the transformation only affects the total entropy and the entropy of the surroundings!

Problem 2

A community (average T=27°C) has an enormous underground reservoir of high-pressure (inert) gas. The reservoir has the following properties:

T= 237 °C
P = 9.95 atm
V= 10^6 m^3
Depth = 2000 m below the surface
Cp = 36 J/(mol K)
Mw= 0.03 kg/mol

Assume that the gas is ideal.

What is the maximum amount of work that the community could extract out of the gas?

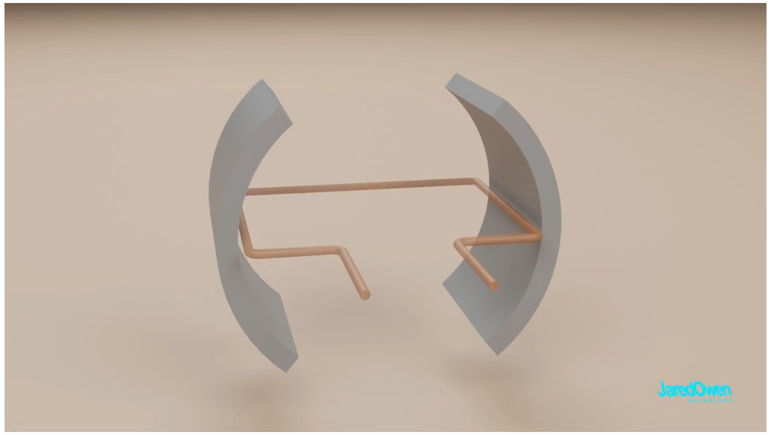
Outline of Part 1: Thermo

Objective: Derive and understand the physical laws that characterize and limit energy conversion systems

- 1st Law of Thermodynamics
  - Internal energy
  - Work
  - Enthalpy
- 2nd Law of Thermodynamics
  - Entropy
  - Reversible and irreversible processes
  - State functions
- Heat to work conversion
  - T-S diagrams
  - Idealized systems (Carnot cycle)
- Real heat to work and work to heat conversion systems
  - Rankine cycles
  - Refrigeration cycles and heat pumps
  - Engines
- Exergy: calculating the maximum work that can be produced/recovered
- **Electrical systems**
  - Electrical machines
  - Fuel cells

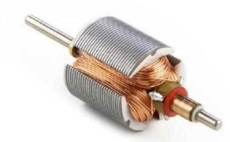
Electric motors

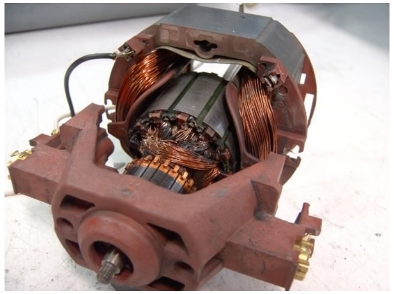
DC motors



Electric motors

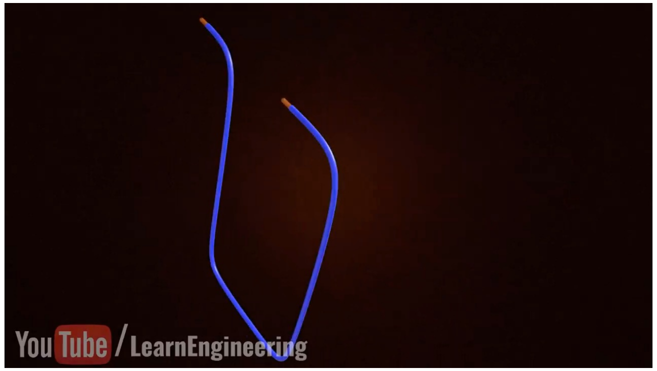
DC motors





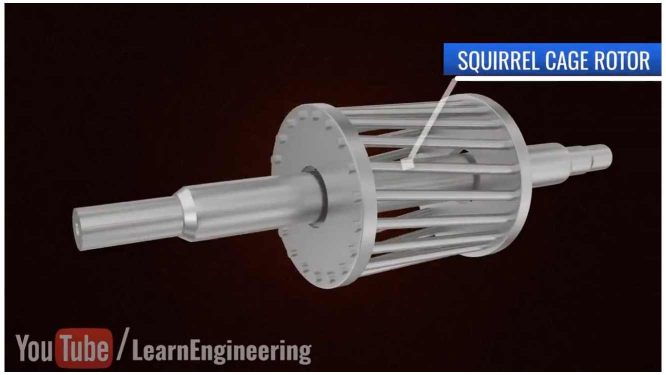
Electric motors

AC induction motors



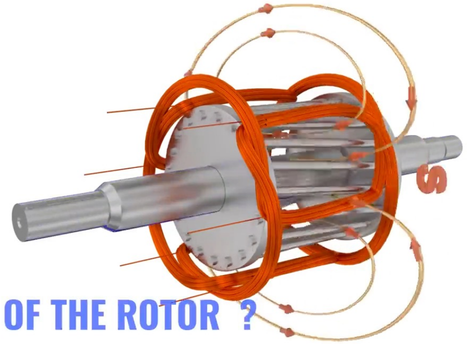
Electric motors

AC induction motors



Electric motors

AC induction motors



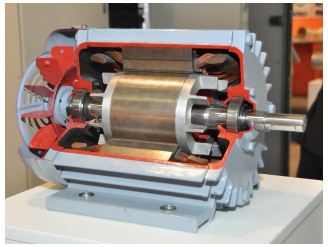
SPEED OF THE ROTOR ?

149

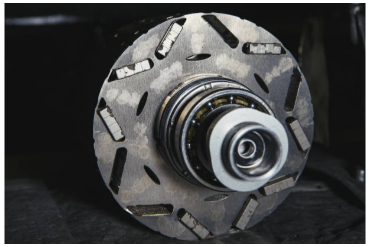
Electric motors

AC motors

A classic induction motor.



Tesla's model 3 rotor
with permanent magnets.



Source: Wikimedia

150

Electric motors

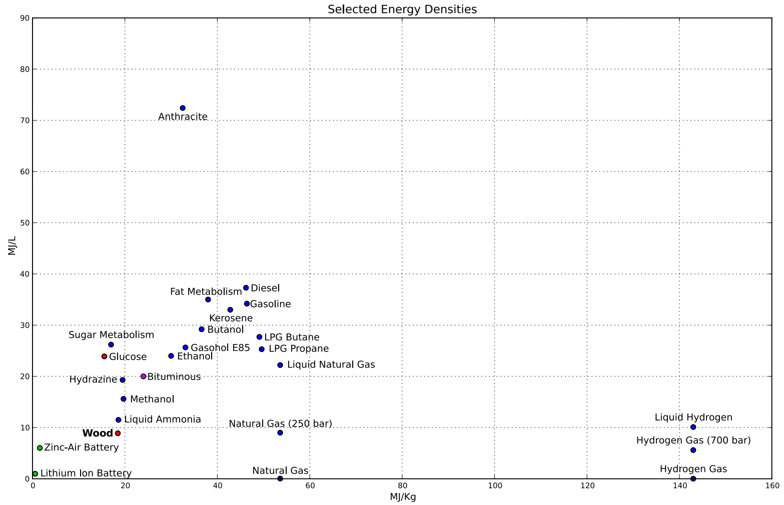
Due to the lack of friction or significant waste heat generated, electric motors are very efficient….

Typical efficiencies are usually above 90%.

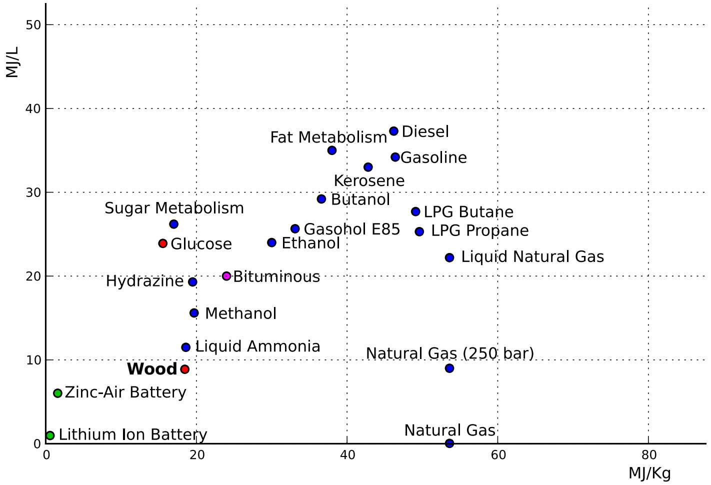
- Best AC induction motors have reached 94% efficiencies
- Tesla's AC permanent magnet Model 3 motor has reportedly reached 96% efficiencies

Why are we even considering other types of motors?

Electric motors: limitations



Electric motors: limitations



Outline of Part 1: Thermo

Objective: Derive and understand the physical laws that characterize and limit energy conversion systems

- 1st Law of Thermodynamics
  - Internal energy
  - Work
  - Enthalpy
- 2nd Law of Thermodynamics
  - Entropy
  - Reversible and irreversible processes
  - State functions
- Heat to work conversion
  - T-S diagrams
  - Idealized systems (Carnot cycle)
- Real heat to work and work to heat conversion systems
  - Rankine cycles
  - Refrigeration cycles and heat pumps
  - Engines
- Exergy: calculating the maximum work that can be produced/recovered
- **Electrical systems**
  - Electrical machines
  - **Fuel cells**

Basics of fuel cells

The idea of fuel cells is to combine the energy density of fuels with electricity generation.

Fuel oxidation involves the exchange of electrons:

$$H_2 + \frac{1}{2} O_2 \rightleftharpoons H_2O$$

This reaction can be separated into two half reactions:

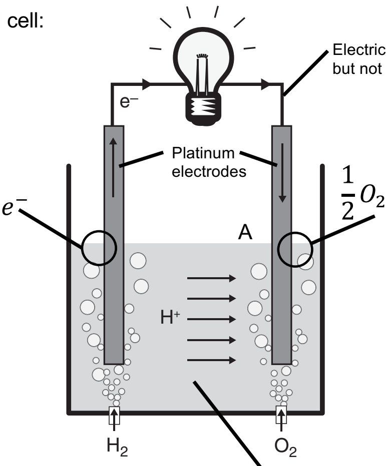
$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

$$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$$

A fuel cells is made by spatially separating these two reactions and forcing the flux of electrons through a conductor to generate a current.

Basics of fuel cells

A simple fuel cell:



Electrical conductor: lets e^- through but not ions.

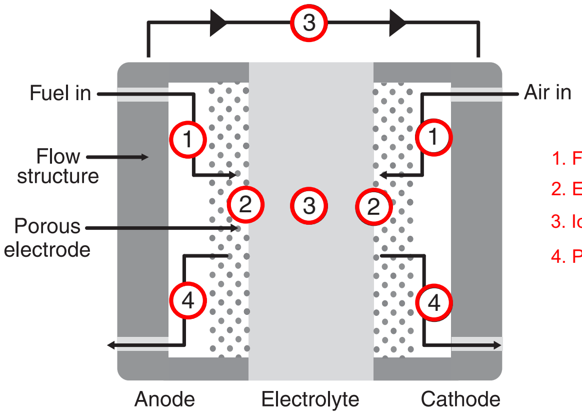
$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

$$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O$$

H_2SO_4 solution: lets ions through but not e^-.

Fuel cells

A real fuel cell:



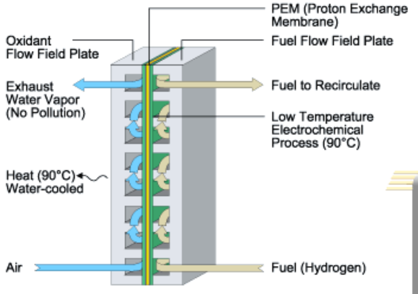
1. Fuel transport
2. Electrochemical reaction
3. Ionic/electronic conduction
4. Product removal

157

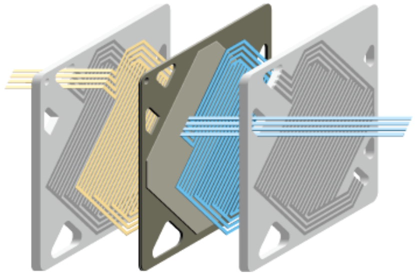
Fuel cells

A commercial H_2 fuel cell:

Schematic:



Actual appearance:



© Ballard fuel cells

158

Thermodynamic potentials

Previously, we had explored the first law in an isolated system and expressed it as:

$$dU = TdS - PdV$$

Mathematically, we can understand this as describing *U* as a function of S and V:

$U(S, V)$ which, in a non isolated system would also depend on *N* (the total number of moles): $U(S, V, N)$

Thinking of U purely as a mathematical function depending on these variables, we can write:

$$dU(S, V, N) = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN$$

Comparing both definitions of U, we can write:

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T \quad \text{and} \quad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -P$$

Finally, the partial derivative of *U* by *N* is often defined as the chemical potential μ:

$$\left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu$$

159

Thermodynamic potentials

Measuring or describing *U* as a function of of entropy and volume is difficult in the lab:

$$dU = TdS - PdV$$

This:

Does not exist…

160

Thermodynamic potentials

Measuring or describing *U* as a function of of entropy and volume is difficult in the lab: $dU = TdS - PdV$

This:

Does exist!

In general extensive properties (which depend on the size of the system) are more difficult to change than intensive properties (that are independent of the size of the system)…

Thermodynamic potentials

Can we describe another thermodynamic potential (a state function that contains the same amount of mathematical information as *U*) that depends on simpler variables to modify?

A mathematical transformation exists that allows us to do this: Legendre transformations.

Starting with: $dU = TdS - PdV$

We use the differential of the variables we want to change and apply the chain rule: $d(PV) = PdV + VdP$

Rearranging: $-PdV = -d(PV) + VdP$

Which we can substitute into the definition of *dU*:

$$dU = TdS - d(PV) + VdP$$

Considering the variation of *U* with *N*: $dU = TdS - d(PV) + VdP + \mu dN$

Thermodynamic potentials

$$dU = TdS - d(PV) + VdP + \mu dN$$

Rearranging, we can make the definition of enthalpy appear:

$$d(U + PV) = dH = TdS + VdP + \mu dN$$

Enthalpy emerges from a mathematical transformation…

We can do a further transformation using de differential of *TS*:

$$d(TS) = TdS + SdT$$

Which rearranges to:

$$TdS = d(TS) - SdT$$

Applied to *dH*, we can get the definition of Gibbs free energy *(G):*

$$d(U + PV - TS) = dG = -SdT + VdP + \mu dN$$

Thermodynamic potentials

Starting with the original definition of *dU*:

$$dU = TdS - PdV$$

We can directly apply the transformation using *TS*:

$$d(TS) = TdS + SdT \quad \text{or} \quad TdS = d(TS) - SdT$$

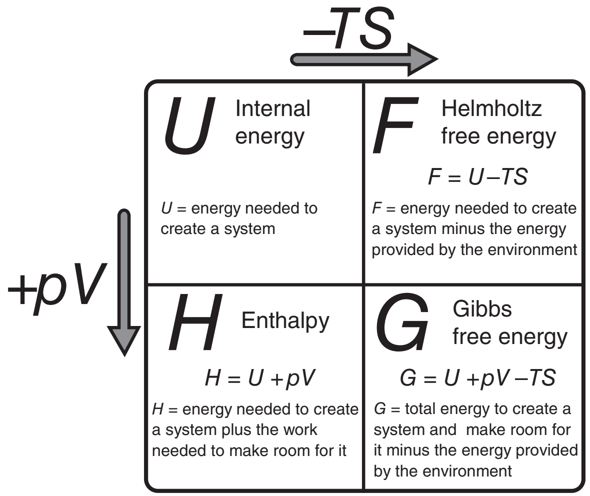
Which leads to the definition of Hemholtz energy (*F*):

$$d(U - TS) = dF = -SdT - PdV + \mu dN$$

PV can be interpreted physically as the work needed to create volume for the system to exist.

Similarly, *TS* can be interpreted as the energy required to be exchanged with the environment by the system.

Thermodynamic potentials



$-TS$

$+pV$

U Internal energy

U = energy needed to create a system

F Helmholtz free energy

$F = U - TS$

F = energy needed to create a system minus the energy provided by the environment

H Enthalpy

$H = U + pV$

H = energy needed to create a system plus the work needed to make room for it

G Gibbs free energy

$G = U + pV - TS$

G = total energy to create a system and make room for it minus the energy provided by the environment

ChE-304 Problem Set 4

Week 4

Problem 1

Massieu (a French mathematician and physicist) proposed alternate thermodynamic potentials based on entropy as a function of internal energy ($dS(U,V,N)$). We don't use them because they are less practical than the ones you are used to seeing. Can you write the 4 "Massieu thermodynamic potentials" with dS being the first and the 3 others obtained using Legendre transformations?

Hint: the goal of the Legendre transforms is to have the variables be functions of intensive variables (in this case T and P). They do not have to be as simple as the classical potentials you are used to.

Fuel cell efficiency

Let's rewrite the first law for fuel cells. In the case of the fuel cell, all non-PV work will end up as electrical work:

$$dU = dQ + dW_{electric} - dW_{PV}$$

In the best case, we will have:

$$dQ = dQ_{rev} = TdS$$

Which would lead to:

$$dU = TdS - dW_{electric} - PdV$$

Using the definition of free energy ($G = U + PV - TS$):

$$dG = dU - SdT - TdS + PdV + VdP = -SdT + VdP - dW_{electric}$$

Fuel cell efficiency

$$dG = -SdT + VdP - dW_{electric}$$

At constant T and P:

$$dG = -dW_{electric}$$

Therefore, in an ideal transformation for a given oxidation, we have:

$$W_{electric} = -\Delta G_{RXN}$$

With this result, we can now think of calculating an efficiency:

$$\eta = \frac{W_{electric}}{Total\ energy}$$

Assuming the input is the full calorific value of the fuel, the efficiency becomes:

$$\eta = \frac{-\Delta G_{RXN}}{-\Delta H_{RXN}}$$

Fuel cell efficiency

$$\eta = \frac{-\Delta G_{RXN}}{-\Delta H_{RXN}}$$

For example, if we take hydrogen oxidation:

$$H_2 + \frac{1}{2} O_2 \rightleftharpoons H_2O$$

$$\Delta G_{RXN} = -237 \ \mathrm{kJ/mol}$$

$$\Delta H_{RXN} = -286 \ \mathrm{kJ/mol}$$

$\Rightarrow$ 83%

Fuel cell efficiency

$$\eta = \frac{-\Delta G_{RXN}}{-\Delta H_{RXN}}$$

This efficiency is not always appropriate to use. To understand why, let's introduce enthalpy in the definition of free energy:

$$G = U + PV - TS = H - TS \Longrightarrow \Delta G = \Delta H - T\Delta S$$

$$\eta = \frac{-\Delta G_{RXN}}{-\Delta H_{RXN}} = \frac{\Delta H_{RXN} - T\Delta S_{RXN}}{\Delta H_{RXN}} = 1 - \frac{T\Delta S_{RXN}}{\Delta H_{RXN}}$$

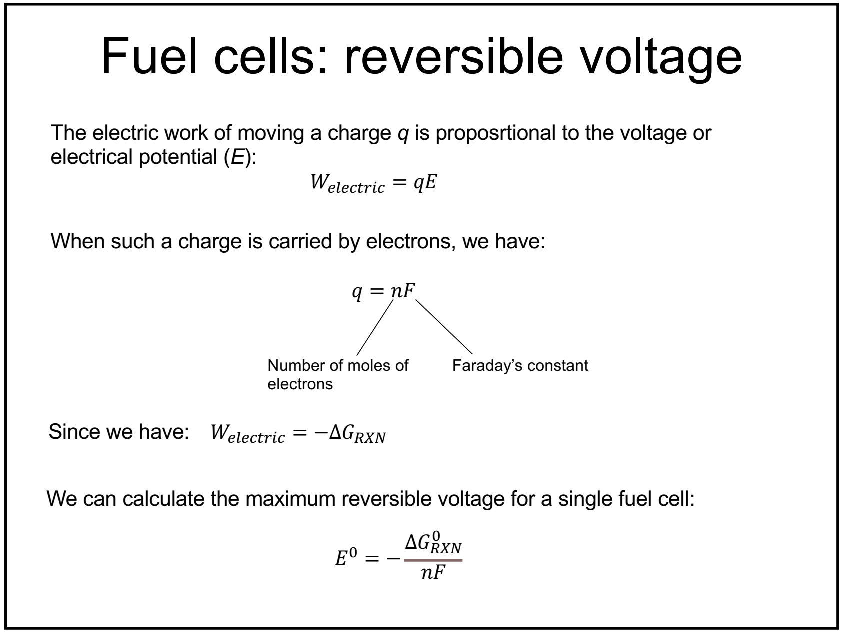
For the rare cases where entropy is positive, we will have an efficiency over 100%!* → There must be something else!

$$\eta = \frac{W_{electric}}{Total \ energy} = \frac{W_{electric}}{Energy\ from\ RX + heat\ received}$$

$$\frac{-\Delta G_{RXN}}{-\Delta H_{RXN} + T\Delta S_{RXN}} = \frac{\Delta H_{RXN} - T\Delta S_{RXN}}{\Delta H_{RXN} - T\Delta S_{RXN}} = 1$$

In cases where heat is being received from the surroundings, this should be included in the efficiency and, by definition, the maximum efficiency will be 100%.

*A fuel oxidation's enthalpy will always be negative, otherwise it will not be a fuel…



Fuel cells: reversible voltage

The electric work of moving a charge *q* is proposrtional to the voltage or electrical potential (*E*):

$$W_{electric} = qE$$

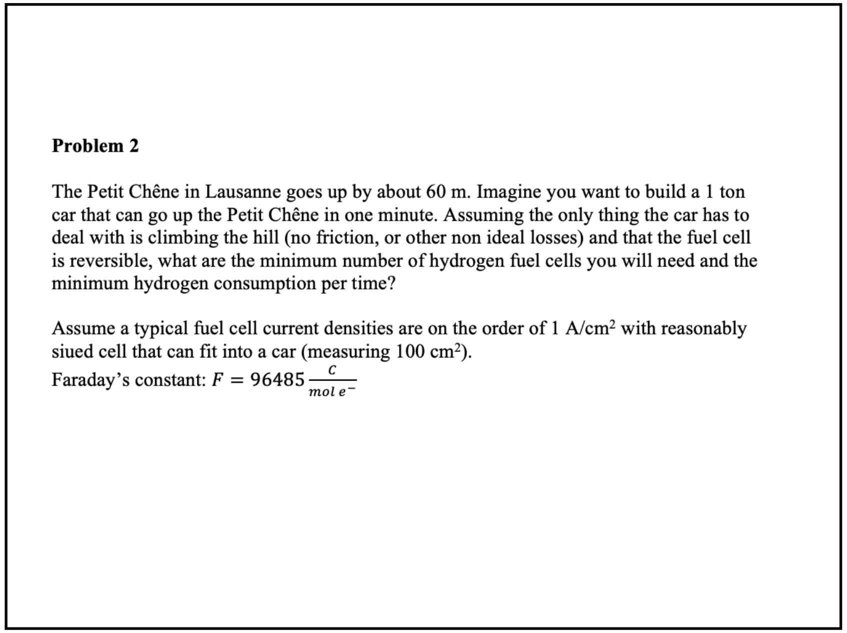
When such a charge is carried by electrons, we have:

$$q = nF$$

Since we have: $W_{electric} = -\Delta G_{RXN}$

We can calculate the maximum reversible voltage for a single fuel cell:

$$E^0 = -\frac{\Delta G^0_{RXN}}{nF}$$



Problem 2

The Petit Chêne in Lausanne goes up by about 60 m. Imagine you want to build a 1 ton car that can go up the Petit Chêne in one minute. Assuming the only thing the car has to deal with is climbing the hill (no friction, or other non ideal losses) and that the fuel cell is reversible, what are the minimum number of hydrogen fuel cells you will need and the minimum hydrogen consumption per time?

Assume a typical fuel cell current densities are on the order of 1 A/cm^2 with reasonably siued cell that can fit into a car (measuring 100 cm^2).
Faraday's constant: $F = 96485 \frac{C}{mol\ e^-}$

Fuel cells

Toyota Mirai

Ballard fuel cell