



Physics I

Lecture 21 -

Heat Engines, Entropy, and The Second Law of Thermodynamics - I

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Outline

1. Heat Engines and The Second Law of Thermodynamics
2. Heat Pumps and Refrigerators
3. Reversible and Irreversible Processes
4. The Carnot Engine
5. Gasoline and Diesel Engines
6. Entropy and Its Changes in Irreversible Processes
7. Entropy on a Microscopic Scale

1. HEAT ENGINES AND THE SECOND LAW OF THERMODYNAMICS

Heat engine: convert heat to work

thermal efficiency of a heat engine e

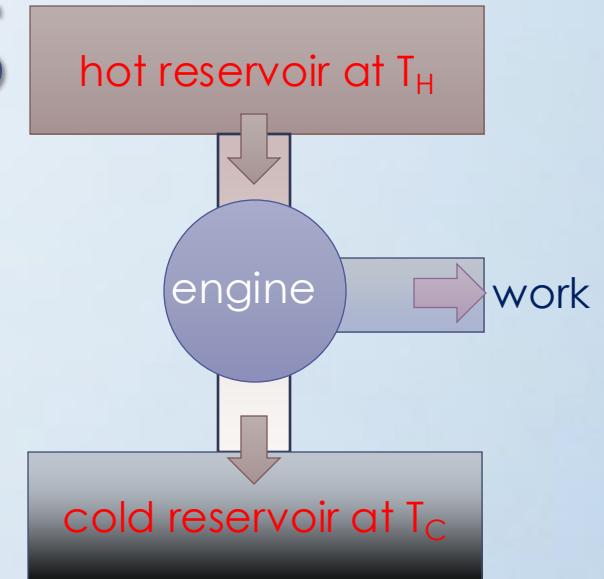
$$e = \frac{\Delta W_{eng}}{|\Delta Q_H|}, \Delta W_{eng} = |\Delta Q_H| - |\Delta Q_C| \rightarrow e = 1 - \frac{|\Delta Q_C|}{|\Delta Q_H|}$$

The second law of thermodynamics (heat-engine statement, Kelvin-Plank statement):

It is impossible to construct a heat engine that, operating in a cycle, produces no effect other than the adsorption of energy from a reservoir and an output of an equal amount of work.

You can not find the efficiency $e = 1, \Delta Q_C = 0$ of an engine.

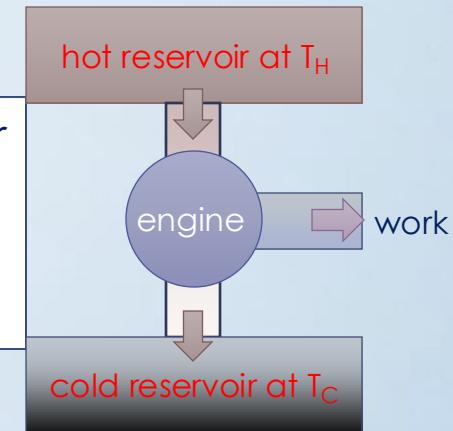
The energy is conserved, $\Delta E = \Delta Q + \Delta W$. The operation of the engine in a cycle shall generate some energy $|\Delta Q_C|$ rejected to the environment.



1. HEAT ENGINES AND THE SECOND LAW OF THERMODYNAMICS

Example: An engine transfers 2.00×10^3 J of energy from a hot reservoir during a cycle and transfers 1.50×10^3 J to a cold reservoir.

- (a) Find the efficiency of the engine.
- (b) How much work does the engine do in one cycle?



(a) $\Delta Q_H = 2.00 \times 10^3$ J, $\Delta Q_C = 1.50 \times 10^3$ J

$$e = 1 - \frac{|Q_C|}{|Q_H|} = 1 - \frac{1.50}{2.00} = 0.250 = 25.0 \%$$

(b) $W = |Q_H| - |Q_C| = 5.0 \times 10^2$ J

2. HEAT PUMPS AND REFRIGERATORS

Heat pump:

The heat and work transferred to the pump are ΔQ_C and ΔW , respectively. The heat energy transferred out of the pump is ΔQ_H .

The coefficient of performance (COP):

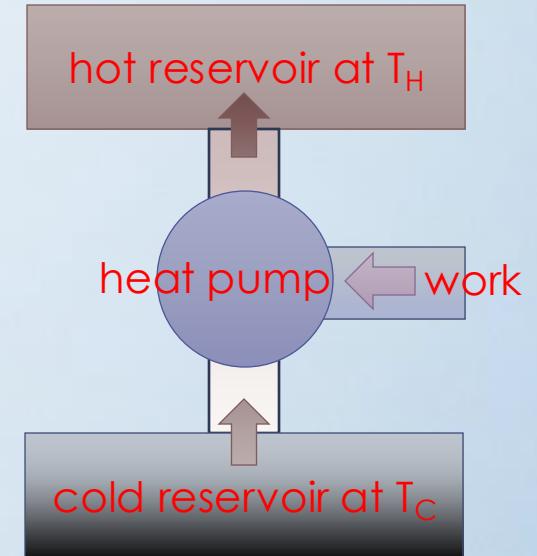
The COP of a refrigerator (or a heat pump) used in a cooling cycle is:

$$COP(\text{cooling mode}) = \frac{|Q_C|}{W}, COP(\text{heating mode}) = \frac{|Q_H|}{W}$$

The second law of thermodynamics (refrigerator statement):

It is impossible for a refrigerator in a cycle to produce only the effect of extracting heat from a cold reservoir and reject the same amount of heat to a hot reservoir. (Clausius Statement)

Energy does not flow spontaneously from a cold to a hot object.



2. HEAT PUMPS AND REFRIGERATORS

Refrigerator:

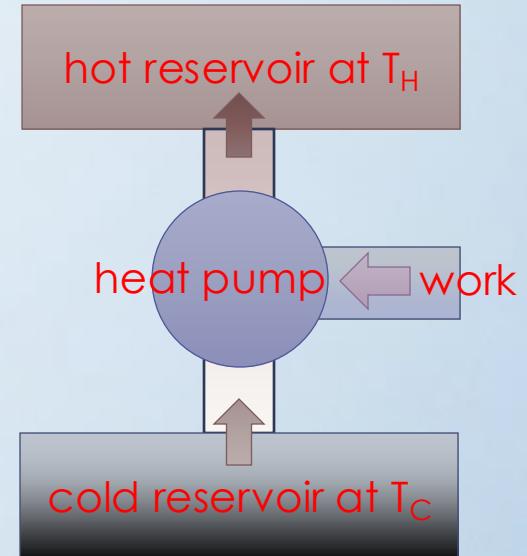
Company	Model	Cooling Power	EER	Energy/Yr
Hitachi	RAS-28	2.8 kW	6.00	413 kWh

$$EER * 1.16 = COP_{cooling} = \frac{|Q_C|}{W}, EER \sim 5 - 6$$

Heat pump:

$$EER * 1.16 = COP_{heating} = \frac{|Q_H|}{W}, EER \sim 4$$

If the outside temperature is -4°C or higher, a typical value of a COP for a heat pump is about 4 (textbook).



3. REVERSIBLE AND IRREVERSIBLE PROCESSES

All natural processes are irreversible.

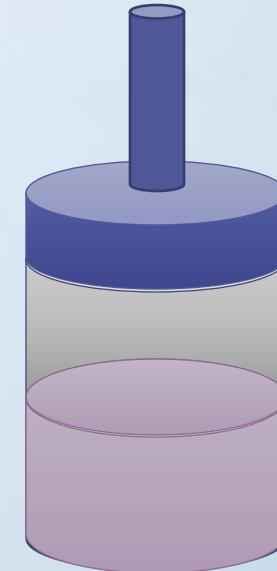
For example, in the free expansion process, the molecules are initially confined in the lower part of the volume. The upper part is in a vacuum and sealed by a membrane. If the membrane is removed, the gas expands to occupy the whole space.

It is possible to confine the gas molecules back to the lower part of the cylinder again but it takes additional energy.

In the reverse process, the gas is compressed and it results in an increase of temperature. The additional energy needs to be transferred to the surroundings.

It is similar in the case as that of the broken of glass. Additional energy is needed for the reverse process.

If the process is varied slowly in equilibrium states, they are almost reversible.



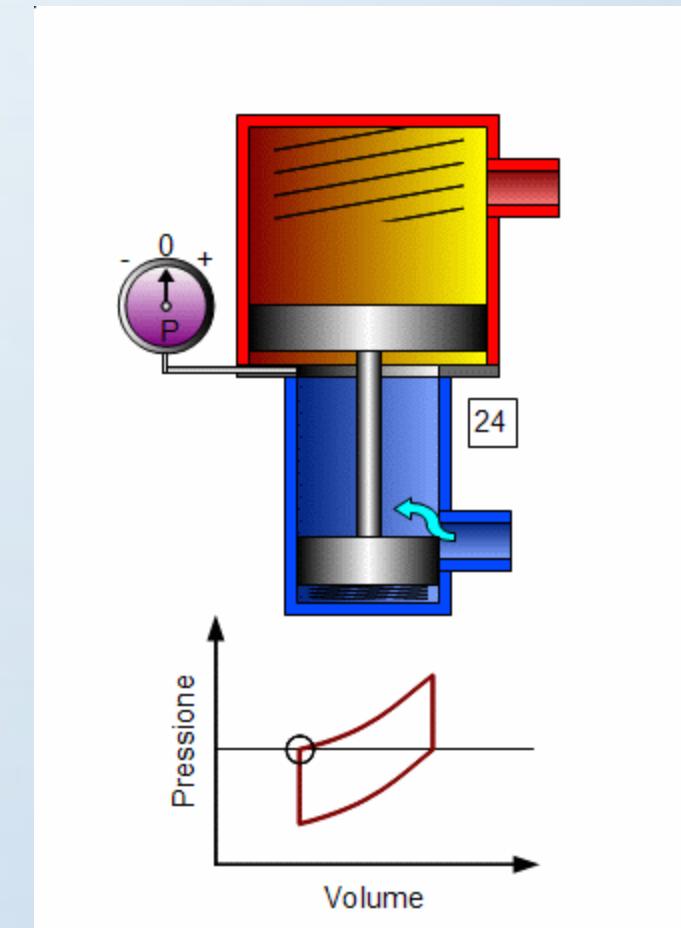
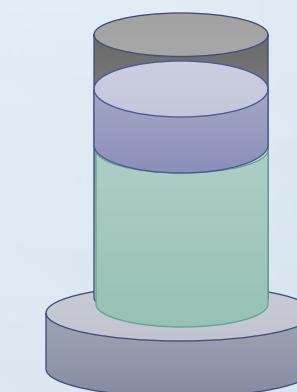
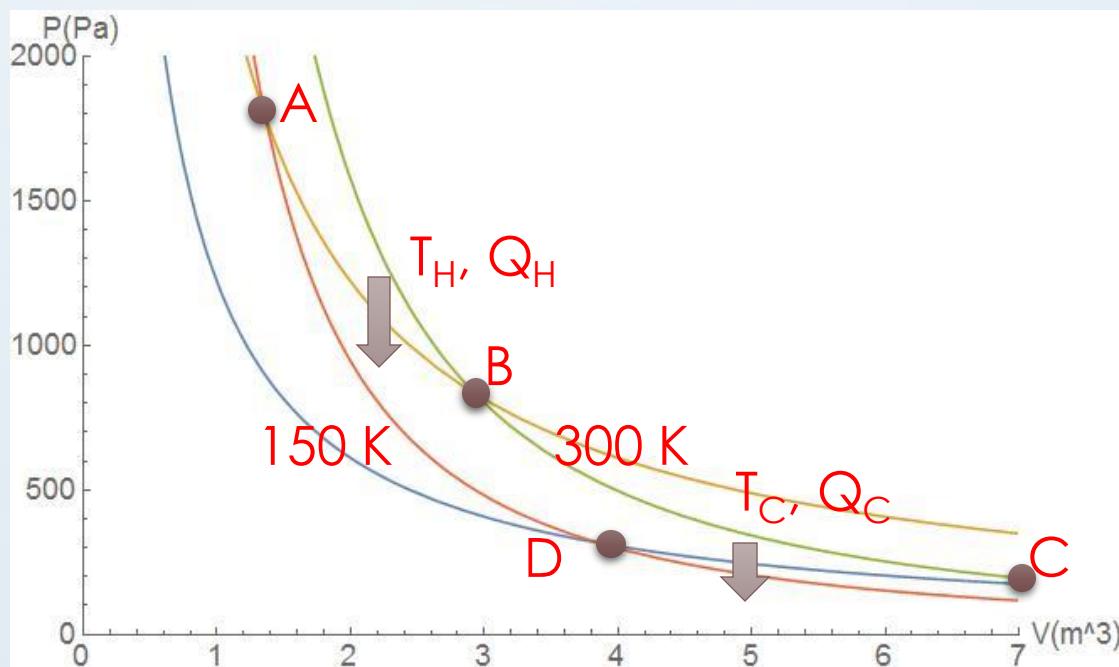
4. THE CARNOT ENGINE

Carnot engine:

No real engine operating between two reservoirs is able to be more efficient than a Carnot engine!!.

Assume that the gas is an ideal gas.

Cylinder walls and the piston are thermally nonconductive.



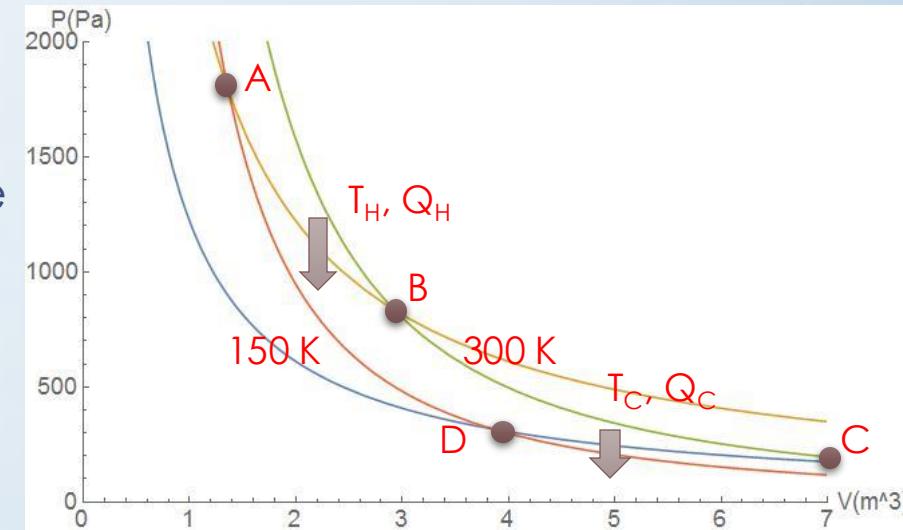
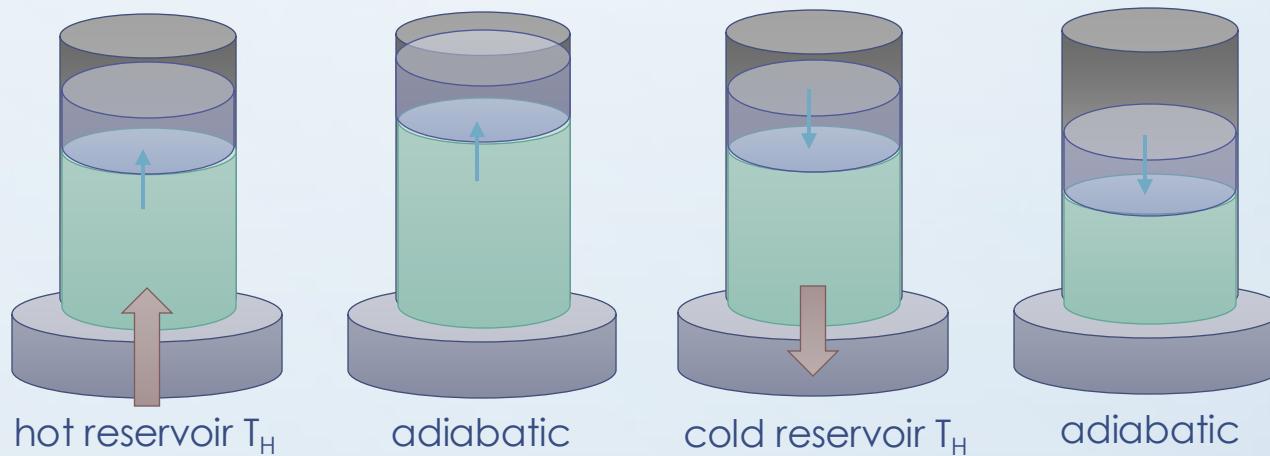
4. THE CARNOT ENGINE

A->B: isothermal, the absorbed heat energy is converted to work

B->C: adiabatic, change temperature from T_H to T_C

C->D: isothermal, the work done on the gas is converted to the expelled heat energy

D->A: adiabatic



4. THE CARNOT ENGINE

Example: In the AB process of the Carnot cycle (1.00 mole of ideal gas with $\gamma = 1.4$), the initial pressure is $1.00 \times 10^5 \text{ Pa}$, the volume is expanded from 0.0200 m^3 to 0.0400 m^3 , (a) How much energy of heat does the gas absorb? (b) In the BC process, if the volume is expanded to 0.0600 m^3 , what is T_C ?

$$P_A = 1.00 \times 10^5 \text{ Pa}, V_A = 0.0200 \text{ m}^3$$

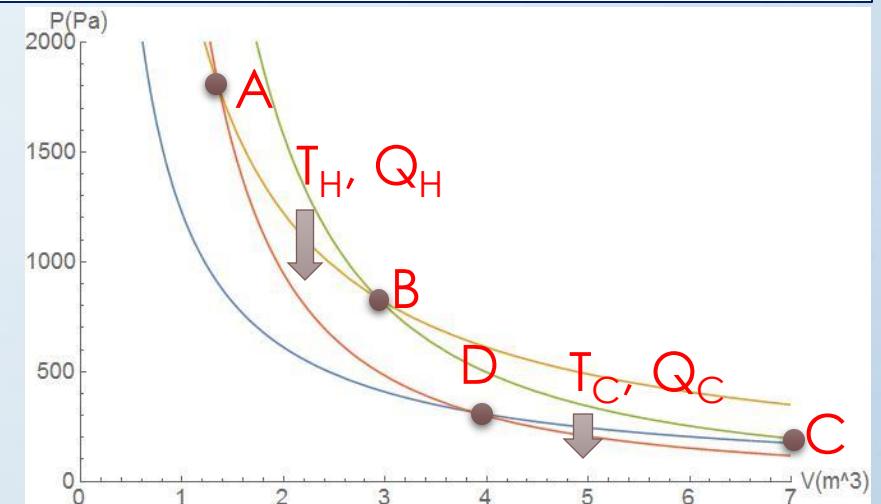
$$V_B = 0.0400 \text{ m}^3, V_C = 0.0600 \text{ m}^3$$

$$Q_H = -W = \int_{V_A}^{V_B} \frac{P_A V_A}{V} dV = 2.00 \times 10^3 \times \ln 2$$

$$Q_H = 1390 \text{ J}$$

$$P_A V_A = n R T_H \rightarrow T_H = \frac{2.00 \times 10^3}{1.00 \times 8.314} = 241 \text{ K}$$

$$T_H V_B^{\gamma-1} = T_C V_C^{\gamma-1} \rightarrow T_C = 241 \times \left(\frac{0.0400}{0.0600} \right)^{0.4} = 205 \text{ K}$$



4. THE CARNOT ENGINE

Thermal efficiency of a Carnot engine:

$$A \rightarrow B: Q_H = \int_{V_A}^{V_B} P dV$$

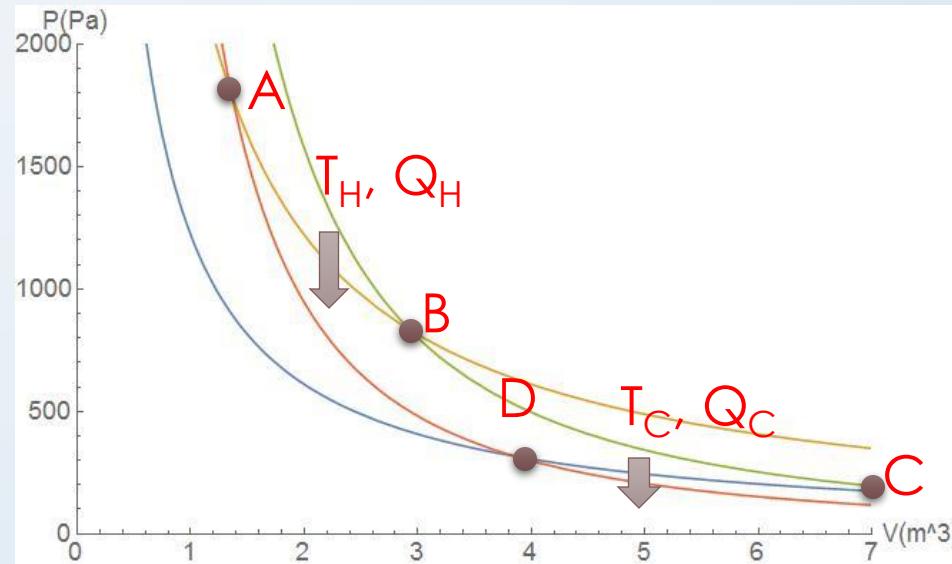
$$Q_H = \int_{V_A}^{V_B} \frac{nRT_H}{V} dV = nRT_H \ln\left(\frac{V_B}{V_A}\right)$$

$$C \rightarrow D: Q_C = \int_{V_C}^{V_D} P dV$$

$$Q_C = \int_{V_C}^{V_D} \frac{nRT_C}{V} dV = -nRT_C \ln\left(\frac{V_C}{V_D}\right)$$

$$T_H V_B^{\gamma-1} = T_C V_C^{\gamma-1} \quad \& \quad T_H V_A^{\gamma-1} = T_C V_D^{\gamma-1} \rightarrow \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

$$e_{Carnot} = 1 - \frac{|Q_C|}{|Q_H|} = 1 - \frac{nRT_C \ln\left(\frac{V_B}{V_A}\right)}{nRT_H \ln\left(\frac{V_C}{V_D}\right)} = 1 - \frac{T_C}{T_H}$$

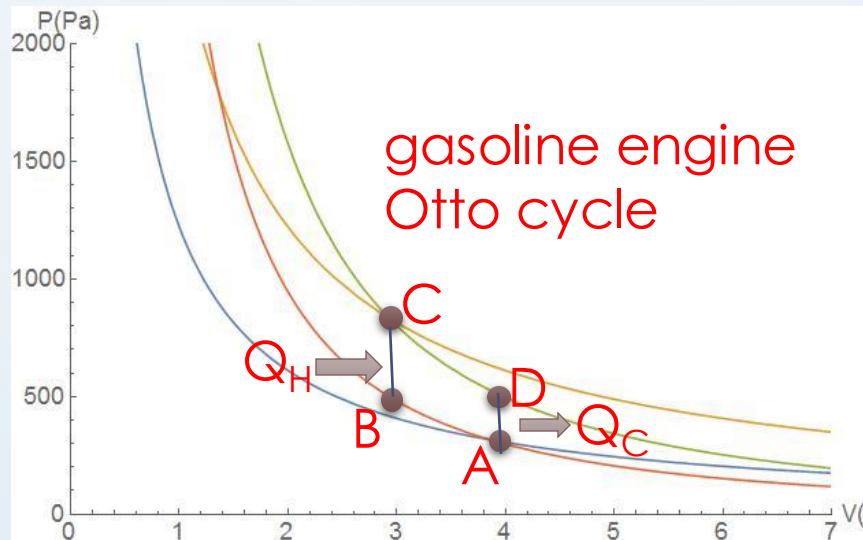


Outline

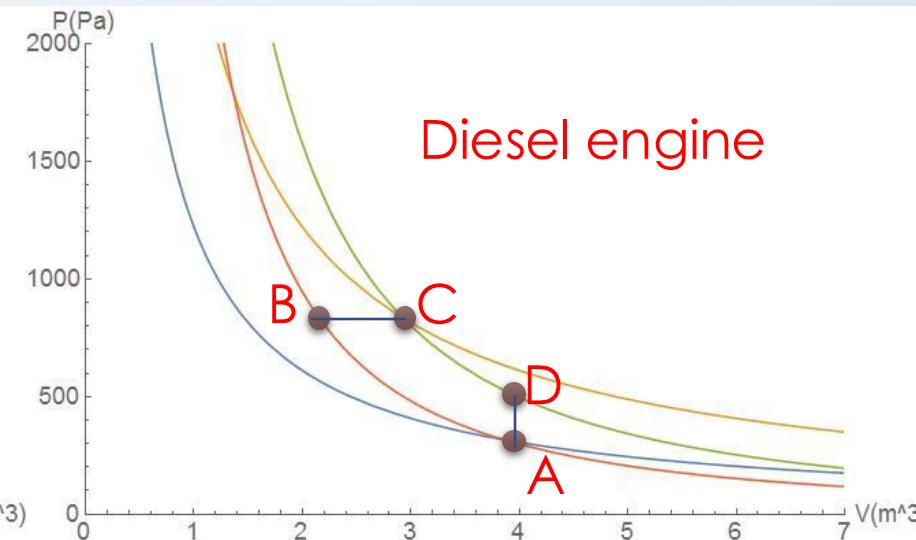
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5. GASOLINE AND DIESEL ENGINES

Gasoline (Otto) engine and Diesel engine:



gasoline engine
Otto cycle



Diesel engine

$$Q_H = nC_V(T_C - T_B)$$

$$Q_H = nC_P(T_C - T_B)$$

$$Q_C = nC_V(T_A - T_D)$$

$$Q_C = nC_V(T_A - T_D)$$

5. GASOLINE AND DIESEL ENGINES

Thermal efficiency of an Otto engine:

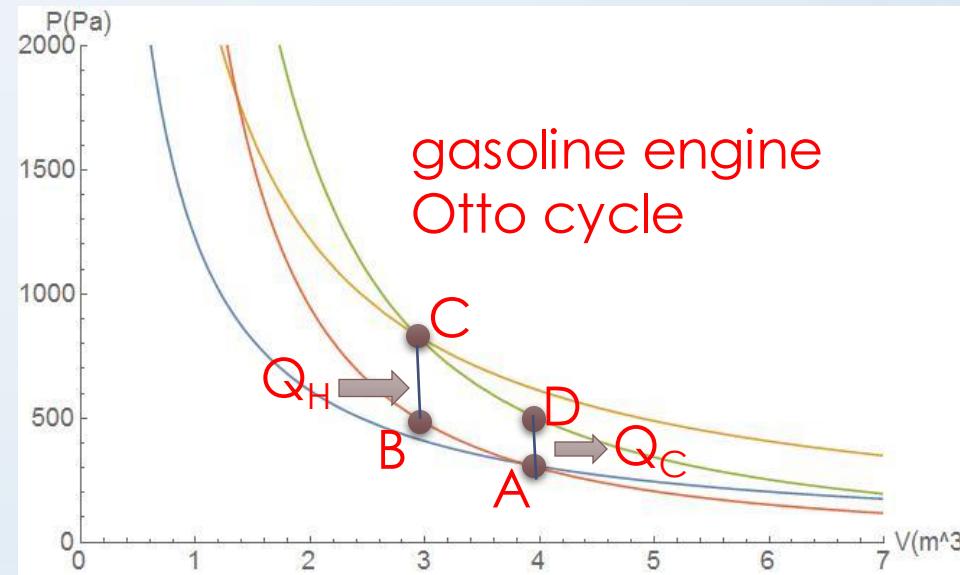
$$Q_H = nC_V(T_C - T_B)$$

$$Q_C = -nC_V(T_D - T_A)$$

$$T_C V_C^{\gamma-1} = T_D V_D^{\gamma-1} \rightarrow T_D = T_C \left(\frac{V_B}{V_A} \right)^{\gamma-1}$$

$$T_B V_B^{\gamma-1} = T_A V_A^{\gamma-1} \rightarrow T_A = T_B \left(\frac{V_B}{V_A} \right)^{\gamma-1}$$

$$e_{otto} = 1 - \frac{|Q_C|}{|Q_H|} = 1 - \frac{T_D - T_A}{T_C - T_B} = 1 - \left(\frac{V_B}{V_A} \right)^{\gamma-1}$$



5. GASOLINE AND DIESEL ENGINES

Example: A n -mol sample of a monatomic ideal gas is taken through the cycle shown in the right figure. At point A, the pressure, volume, and temperature are P_i , V_i , and T_i , respectively. In terms of R and T_i , find (a) the total energy entering the system by heat per cycle, (b) the work delivered by the system per cycle, (c) the efficiency of the engine.

Isothermal process: $\Delta E = 0, \Delta Q = -\Delta W = \int PdV, PV = \text{const}$

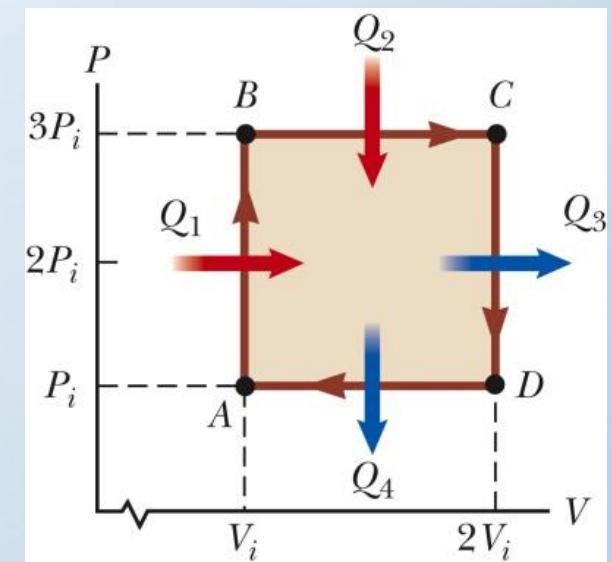
Adiabatic process: $\Delta Q = 0, \Delta E = \Delta W = nC_V\Delta T, PV^\gamma = \text{const}$

Isovolumetric process: $\Delta W = 0, \Delta E = \Delta Q = nC_V\Delta T, V = \text{const}$

Isobaric process: $\Delta E = \Delta Q + \Delta W, \Delta Q = nC_P\Delta T, \Delta W = -P\Delta V, P = \text{const}$

Monatomic ideal gas $\rightarrow C_V = \frac{3}{2}R, C_P = \frac{5}{2}R, T_A = T_i$

Monatomic ideal gas $\rightarrow T_B = 3T_i, T_C = 6T_i, T_D = 2T_i$



5. GASOLINE AND DIESEL ENGINES

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Monatomic ideal gas $\rightarrow C_V = \frac{3}{2}R$, $C_P = \frac{5}{2}R$, $T_A = T_i$, $T_B = 3T_i$, $T_C = 6T_i$, $T_D = 2T_i$

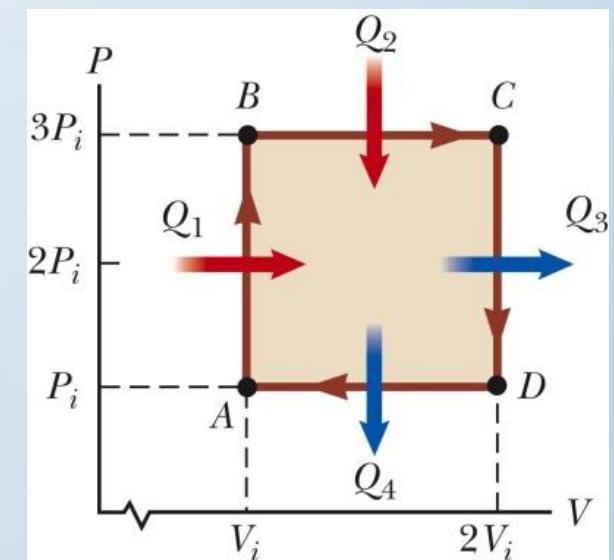
$$(a) A \rightarrow B: \Delta Q = nC_V\Delta T = n \cdot \frac{3}{2}R \cdot 2T_i = 3nRT_i$$

$$B \rightarrow C: \Delta Q = nC_P\Delta T = n \cdot \frac{5}{2}R \cdot 3T_i = \frac{15}{2}nRT_i$$

$$C \rightarrow D: \Delta Q = nC_V\Delta T = n \cdot \frac{3}{2}R \cdot (-4T_i) = -6nRT_i$$

$$D \rightarrow A: \Delta Q = nC_P\Delta T = n \cdot \frac{5}{2}R \cdot (-T_i) = -\frac{5}{2}nRT_i$$

Total energy entering the system by heat is $2nRT_i$.



5. GASOLINE AND DIESEL ENGINES

Example: A n -mol sample of a monatomic ideal gas is taken through the cycle shown in the right figure. At point A, the pressure, volume, and temperature are P_i , V_i , and T_i , respectively. In terms of R and T_i , find (a) the total energy entering the system by heat per cycle, (b) the work delivered by the system per cycle, (c) the efficiency of the engine.

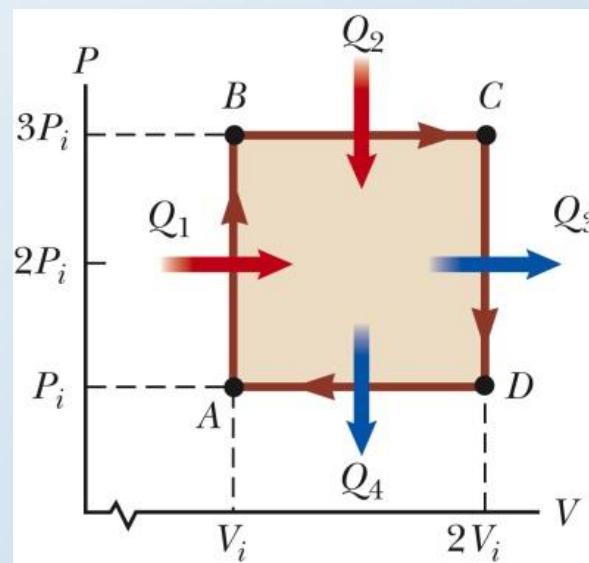
Monatomic ideal gas $\rightarrow C_V = \frac{3}{2}R$, $C_P = \frac{5}{2}R$, $T_A = T_i$, $T_B = 3T_i$, $T_C = 6T_i$, $T_D = 2T_i$

(b) B \rightarrow C: $\Delta W = -P\Delta V = -3P_i \cdot V_i$

D \rightarrow A: $\Delta W = -P\Delta V = -P_i(-V_i) = P_iV_i$

$\Delta W_{total} = -2P_iV_i = -2nRT_i$

(c) $e = \left| \frac{\Delta W}{\Delta Q_1 + \Delta Q_2} \right| = \left| \frac{-2nRT_i}{10.5nRT_i} \right| = \frac{4}{21} = 19\%$



6. ENTROPY AND ITS CHANGES IN IRREVERSIBLE PROCESSES

Isothermal expansion gives you the second type of heat. This type of heat is correlated with the change of microstates. Here we define the change of microstates as entropy variation:

$$\Delta S = \frac{\Delta Q}{T}$$

In the Carnot engine: $\frac{|\Delta Q_c|}{T_c} = \frac{|\Delta Q_H|}{T_H}$, $Q_H > 0$ & $Q_c < 0 \rightarrow \frac{Q_H}{T_H} + \frac{Q_c}{T_c} = 0$

For any reversible cycles, the change of entropy is zero in a cycle.

$$\sum \Delta S_i = \sum \frac{\Delta Q_i}{T_i}$$

The first type of heat is generated by a temperature variation. The second type of heat is generated by the increase of entropy.

6. ENTROPY AND ITS CHANGES IN IRREVERSIBLE PROCESSES

Entropy and the second law of thermodynamics: The entropy of the Universe increases in all natural processes. You may consider the oil or coal that we consume in our daily life.

$$\Delta S = \sum \Delta S_i = \int dS = \int_i^f \frac{dQ}{T}$$

In a reversible and adiabatic process, the entropy change gives

$$\Delta S = 0 \rightarrow \oint \frac{dQ}{T} = 0$$

Example: A solid substance has a latent heat of fusion L_f melts at a temperature T_m . Calculate the change in entropy when a mass m of this substance is melted.

$$\Delta Q = mL_f, T = T_m$$

$$\Delta S = \frac{\Delta Q}{T_m} = \frac{mL_f}{T_m}$$

6. ENTROPY AND ITS CHANGES IN IRREVERSIBLE PROCESSES

Calculation of the change of entropy:

The change of entropy in isothermal expansion or free expansion:

$$E = nC_V T, PV = nRT, \Delta E = \Delta Q + \Delta W$$

$$\Delta E = 0 \rightarrow \Delta Q = -\Delta W = P\Delta V$$

$T = \text{const}$ for isothermal or free expansion process

$$\Delta S = \frac{\Delta Q}{T} = \frac{1}{T} \int_{V_i}^{V_f} P dV = \frac{1}{T} \int_{V_i}^{V_f} \frac{nRT}{V} dV = nR \ln\left(\frac{V_f}{V_i}\right)$$

The change of entropy in other processes:

$$\Delta Q = \Delta E - \Delta W = \Delta E + P\Delta V$$

$$\Delta S = \frac{\Delta E}{T} + \frac{P\Delta V}{T} = \int_{T_i}^{T_f} \frac{nC_V dT}{T} + \int_{V_i}^{V_f} \frac{1}{T} \frac{nRT}{V} dV = nC_V \ln\left(\frac{T_f}{T_i}\right) + nR \ln\left(\frac{V_f}{V_i}\right)$$

6. ENTROPY AND ITS CHANGES IN IRREVERSIBLE PROCESSES

Example: Suppose that 1 mol of an ideal gas undergoes a free expansion to four times its initial volume. Please calculate the entropy changes.

$n = 1, \Delta E = 0$, assume initial volume $V_i, V_f = 4V_i$

$$\Delta S = \int_{V_i}^{V_f} \frac{R}{V} dV = R \ln \left(\frac{V_f}{V_i} \right) = R \ln 4$$

6. ENTROPY AND ITS CHANGES IN IRREVERSIBLE PROCESSES

Entropy change in a constant-pressure process:

$$\Delta Q = nC_P \Delta T \rightarrow \Delta S = \int_{T_i}^{T_f} \frac{nC_P dT}{T} = nC_P \ln\left(\frac{T_f}{T_i}\right)$$

Entropy change in an inelastic collision:

$$\Delta S = \frac{\Delta Q}{T} = \frac{mgh}{T}$$



Entropy change in heat conduction from a hot to a cold reservoir:

$$\Delta Q_H = \Delta Q_C = \Delta Q \rightarrow \Delta S = \frac{\Delta Q}{T_C} - \frac{\Delta Q}{T_H}$$

Entropy change in a Carnot cycle:

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

7. ENTROPY ON A MICROSCOPIC SCALE

The entropy is a measure of the disorder of a macroscopic state of the system. Entropy can be defined using the macroscopic concepts of heat and temperature. On the other hand, the entropy is correlated with the change of microstates.

Suppose the gas occupies volume V_i initially and then expands to fill V_f . Assume each molecule occupies a microscopic volume v_m .

The number of possible initial microstates for N molecules is $W_i = (V_i/v_m)^N$. The initial entropy is $S_i = k_B \ln W_i = Nk_B \ln(V_i/v_m)$.

The number of possible final microstates for N molecules is $W_f = (V_f/v_m)^N$. The final entropy is $S_f = k_B \ln W_f = Nk_B \ln(V_f/v_m)$.

$$\Delta S = S_f - S_i = Nk_B \ln \left(\frac{V_f}{V_i} \right) = nR \ln \left(\frac{V_f}{V_i} \right)$$

EXERCISE

A sample of an ideal gas (n moles at a temperature T) expands isothermally, doubling in volume. Show that the work done on the gas in expanding is $W = -nRT \ln(2)$.

$$PV = nRT$$

$$P(V) = \frac{nRT}{V}$$

$$W = - \int_{V_0}^{2V_0} P dV = - \int_{V_0}^{2V_0} \frac{nRT}{V} dV = -nRT \ln\left(\frac{2V_0}{V_0}\right)$$

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