Lecture 21 Heat Engines, Entropy, and the Second Law of Thermodynamics

1. The Zeroth Law of Thermodynamics: equilibrium -> the same T
2. The First Law of Thermodynamics: dE = dQ + dW => adiabatic, isobaric, isovolumetric, isothermal

21.1 Heat Engines and the Second Law of Thermodynamics

Basic definition of e:

$$e = \frac{W_{eng}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$$

(for different engines you may derive the dependence of e by other parameters, e.g. T or …)

The second law of thermodynamics (heat-engine 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 the performance of an equal amount of work. (Kelvin Statement)

You can not find the efficiency e = 1 (Q_c = 0) of an engine.

dE = dQ + dW for one direction of thermodynamic process, the energy is conserved, for a cycle of thermodynamic process, you definitely lose some energy or work, converting to heat -> irreversible

Example: The Efficient of an Engine
An engine transfers 2.00 x 10^3 J of energy from a hot reservoir during a cycle and transfers 1.50 x 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?
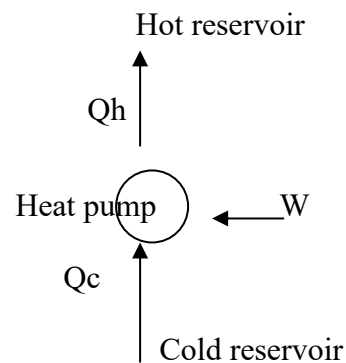
$$e = 1 - \frac{1.5}{2} = 25\% , \quad W = (2 - 1.5) \cdot 10^3 J$$
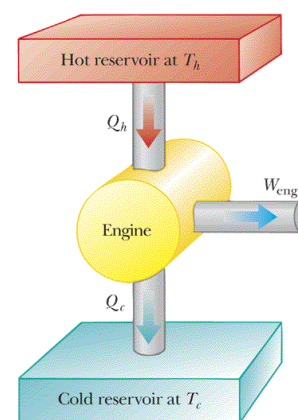
21.2 Heat Pumps and Refrigerators

Hot reservoir

Qh

Heat pump ◯ ◄——W

Qc

Cold reservoir

The heat and work transferred to the system are Q_c and W, respectively.   The heat energy transferred out of the pump is Q_h.

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

$$COP(cooling\_\bmod e) = \frac{|Q_c|}{W}, \quad COP_{Carnot} = \frac{T_c}{T_h - T_c},$$

the greater the COP, the better the refrigerator.

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 object and reject the same amount of heat to a hot object. (Clausius Statement)

Clausius statement of the second law: Energy does not flow spontaneously from a cold object to a hot object.

21.3 Reversible and Irreversible Processes

There are many irreversible processes that cannot be described by the heat-engine or refrigerator statements of the second law, such as a glass falling to the floor and breaking or a balloon popping. However, all irreversible processes have one thing in common – the system plus its surroundings moves toward a less ordered state.

Irreversible process: they occur naturally in only one direction -> energy minimum? limited efficiency of a heat engine -> a machine capable of continuously converting internal energy in a cyclic process completely to other forms of energy cannot be constructed.

reversible process: one for which the system can be returned to its initial condition

along the same path and for which every point along the path is an equilibrium state.

A general characteristic of a reversible process is that no dissipative effects (such as turbulence or friction) that convert mechanical energy to internal energy can be present.

irreversible process: a process that does not satisfy these requirements, most natural processes are known to be irreversible.
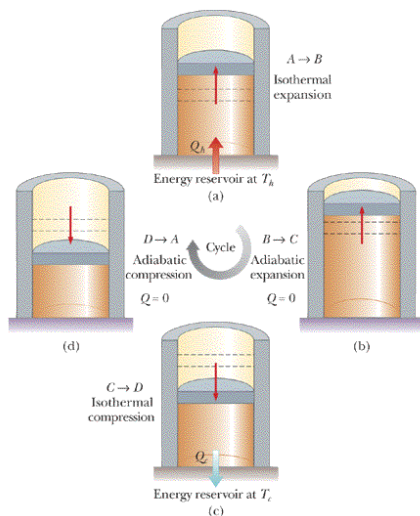
Real processes proceed in a preferred direction – irreversible.

21.4 The Carnot Engine

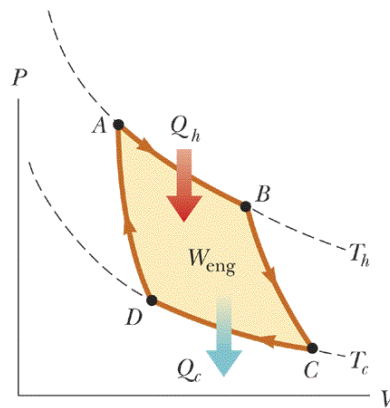1824 , a French engineer Sadi Carnot described a theoretical engine
The net work done by a working substance taken through the Carnot cycle is the greatest amount of work possible for a given amount of energy supplied to the substance at the upper temperature.

1. Assume **an ideal gas**
2. Cylinder walls and the piston are thermally nonconductive.
The process:
A->B isothermal – adsorbs energy Q_h and does work W_{AB} at T_h,
B->C adiabatic, temperature from T_h to T_c and does work W_{BC},
C->D isothermal – expels energy Q_c and the work done on the gas is W_{CD} at T_c,
D->A adiabatic, temperature from T_c to T_h and the work done on the gas is W_{DA},

$$\frac{|Q_c|}{|Q_h|} = \frac{T_c dS}{T_h dS} = \frac{T_c}{T_h}, \quad e_c = 1 - \frac{T_c}{T_h}$$

The efficiency is zero if $T_c = T_h$.
The efficiency is 1 if $T_c = 0$.
All real engines are less efficient than the Carnot engine because they all operate irreversibly in order to complete a cycle in a brief time period.

Example: In the AB process of the Carnot cycle (1 mole of ideal gas with $\gamma = 1.4$), the initial pressure is 1×10^5 Pa, the volume is expanded from 0.02 m^3 to 0.04 m^3, (a) How much energy of heat (Q_h) does the gas absorb? (b) In the BC process, if the volume is expanded to 0.06 m^3, what is Tc?

$$T_h = \frac{P_i V_i}{nR} = 240.55K, \quad Q_h = -W = \int PdV = \int_{0.02}^{0.04} \frac{2000}{V} dV = 2000[\ln V]_{0.02}^{0.04} = 1386$$

$$T_c = T_h \left(\frac{V_h}{V_c}\right)^{\gamma-1} = 240.55 \cdot \left(\frac{0.04}{0.06}\right)^{0.4} = 204.5K$$

Why $\frac{\Delta Q_h}{\Delta Q_c} = \frac{T_h}{T_c}$?

A→B $\quad \Delta Q_h = Q_h = -W = \int_{V_A}^{V_B} \frac{nRT_h}{V} dV = nRT_h \ln\left(\frac{V_B}{V_A}\right)$

D→C $\quad \Delta Q_C = Q_c = -W = \int_{V_D}^{V_C} \frac{nRT_h}{V} dV = nRT_h \ln\left(\frac{V_C}{V_D}\right)$

$$\frac{\Delta Q_h}{\Delta Q_c} = \frac{T_h}{T_c} \frac{\ln(V_B/V_A)}{\ln(V_C/V_D)}, \quad V_B^{\gamma-1}T_h = V_C^{\gamma-1}T_C \rightarrow V_B = \left(\frac{T_C}{T_h}\right)^{1/(\gamma-1)} V_C$$

$$V_A = \left(\frac{T_C}{T_h}\right)^{1/(\gamma-1)} V_D \rightarrow \ln(V_B/V_A) = \ln(V_C/V_D) \rightarrow \frac{\Delta Q_h}{\Delta Q_c} = \frac{T_h}{T_c}$$

What can we obtained from the PV diagram for the Carnot cycle?

AB process (isothermal at a temperature of T_h):

$$P_A V_A = nRT_h = P_B V_B,$$

$$Q_h = \Delta Q_h = T_h \Delta S = -\Delta W = \int_{VA}^{VB} P dV = \int_{VA}^{VB} \frac{nRT_h}{V} dV$$

BC process (adiabatic, temperature variation from T_h to T_c)

$$P_B V_B^{\gamma} = P_C V_C^{\gamma}, \text{ if we know } T_h, \text{ we can calculate } T_c$$
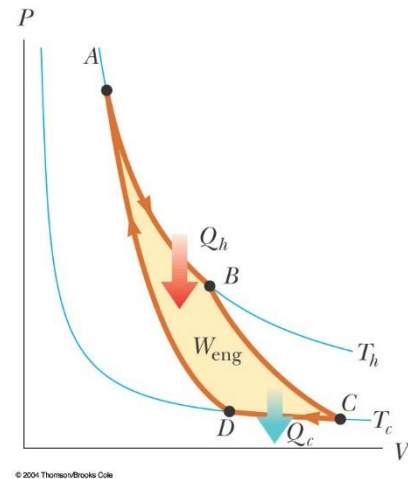
CD process (isothermal at T_c)

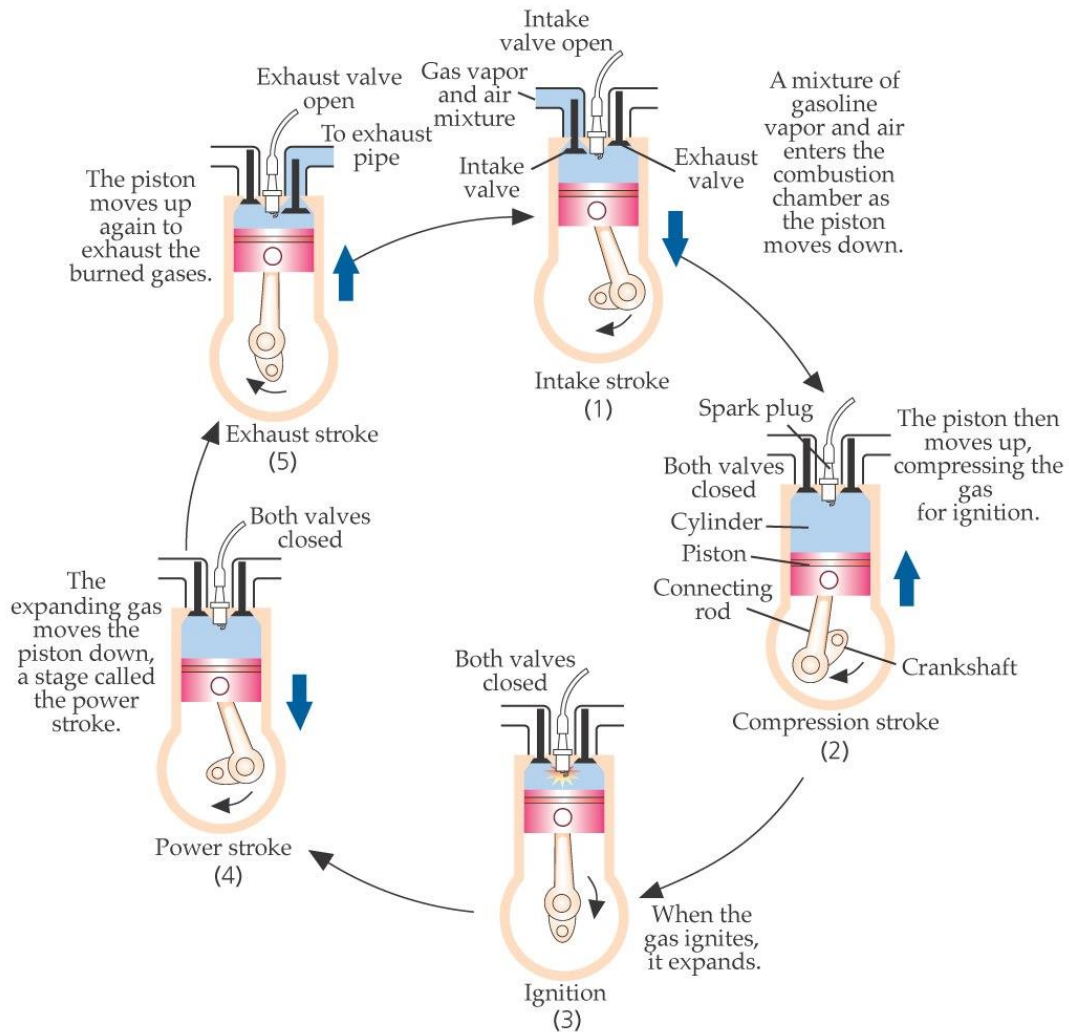$$Q_c = \int_{VC}^{VD} \frac{nRT_c}{V} dV = T_c \frac{Q_h}{T_h}$$

DA process (adiabatic, from T_c to T_h)
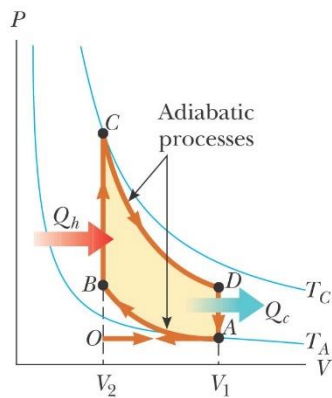
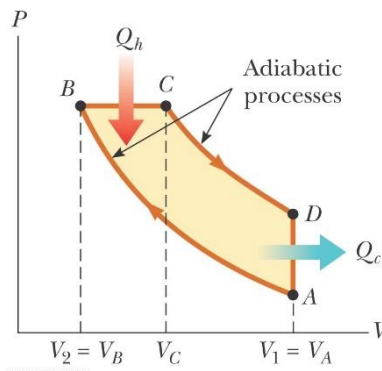Work done in the ABCDA cycle?

$$W = Q_h - Q_c$$

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21.5 Gasoline and Diesel Engines

Gasoline and Diesel Engine

| PV diagram for the Otto cycle | PV diagram for an ideal diesel engine |

Left: $Q_h = nC_V\Delta T$, $Q_c = nC_V\Delta T$ Right: $Q_h = nC_P\Delta T$, $Q_c = nC_V\Delta T$

21.6 Entropy

a state variable: entropy – S

the Carnot engine: $\dfrac{|Q_c|}{T_c} = \dfrac{|Q_h|}{T_h}$, $\dfrac{Q_h}{T_h} + \dfrac{Q_c}{T_c} = 0$, $\sum \dfrac{Q}{T} = 0$

this equation is true for any reversible cycles

consider any infinitesimal process, $dS = \dfrac{dQ_r}{T}$ the heat is to be determined along a

reversible process

When heat is absorbed by the system, dQ_r is positive and hence the entropy increase. When thermal energy is expelled by the system, dQ_r is negative and the entropy decrease.
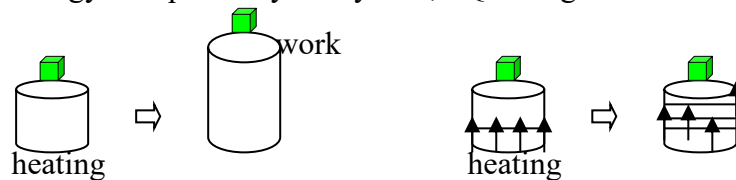
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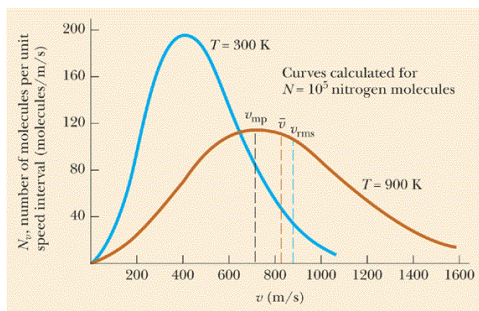
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Entropy and the second law of thermodynamics
The entropy of the Universe increases in all natural processes.   Consider the oil or coal that we consume in our life.

$$\Delta S = \int_i^f dS = \int_i^f \frac{dQ_r}{T}$$

reversible and adiabatic process -> isentropic process
$\Delta S = 0$

$$\oint \frac{dQ_r}{T} = 0$$

Example: Change in Entropy – Melting
A solid substance has a latent heat of fusion Lf melts at a temperature Tm.   Calculate

the change in entropy when a mass m of this substance is melted.

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

21.7 Entropy change in irreversible process:

Isothermal expansion gives $\Delta S > 0$.

The total entropy of an isolated system that undergoes a change cannot decrease.

1. Entropy of an ideal gas:

$$dS = \frac{dQ_{rev}}{T}, \quad dE_{int} = dQ_{rev} + dW = dQ_{rev} - PdV$$

$$E = \frac{3}{2}nRT \ \rightarrow \ dE = nC_V dT$$

$$dS = \frac{dE + PdV}{T} = \frac{nC_V dT + PdV}{T} = \frac{nC_V dT + \dfrac{nRT}{V}dV}{T}$$

$$\Delta S = \int dS = nC_V \int \frac{dT}{T} + nR \int \frac{dV}{V} = nC_V \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right)$$

2. Entropy Change in an isothermal expansion:

$$\Delta S = \int dS = nC_V \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right) = nR\ln\left(\frac{V_2}{V_1}\right)$$

$$Q = T\Delta S = nRT\ln\left(\frac{V_2}{V_1}\right)$$

3. Entropy change in a free expansion:

Definition of free expansion: W = 0 at walls, Q = 0 at walls,

$E_i = E_f \Rightarrow T_i = T_f$

dE = 0 for the whole system, no net energy is delivered to the system through the wall, dW + dQ = 0 for the system

$$\Delta S = \frac{1}{T}\int dQ = \frac{1}{T}\int PdV = nR\ln\left(\frac{V_f}{V_i}\right)$$

Insulating wall

Vacuum

Membrane

Gas at T_i

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Example:

Suppose that 1 mol of an ideal gas undergoes a free expansion to four times its initial volume.   (a) Calculate the entropy changes.   (b) Calculate the entropy from that of microstates.

$$\Delta S = R \ln(\frac{V_f}{V_i}) = R \ln 4$$

$$\Delta S = S_f - S_i = k_B N_A \ln\left(\frac{V_f}{V_m}\right) - k_B N_A \ln\left(\frac{V_i}{V_m}\right) = R \ln 4$$

Entropy change in a constant-pressure process:

$$dQ = nC_P dT, \quad dS = \frac{dQ}{T} = nC_P \frac{dT}{T}$$

Entropy change in an inelastic collision:

$$\Delta S = \frac{Q_{rev}}{T} = \frac{mgh}{T}$$

Entropy change in heat conduction from one reservoir to another:

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

Entropy change in a Carnot cycle:

$$\left|\Delta S_H\right| = \left|\frac{Q_H}{T_H}\right| = \left|\Delta S_C\right| = \left|\frac{Q_C}{T_C}\right|$$

21.8 Entropy on a Microscopic Scale

What is entropy in microscopic viewpoints?   What is internal energy?

The importance of entropy grew tremendously as the field of physics called statistical mechanics.   Entropy isolated systems tend toward disorder, an entropy is a measure of that disorder.

The two dices system: the macrostate corresponds to the sum of numbers of the two dices.   The low probability macrostate of 2 has only one possible microstate of 1 – 1.   The high probability microstate of 7 has size possible microstates.   High probability macrostates are disordered macrostates, and low probability macrostates are ordered macrostates;

All physical processes tend toward more probable states for the system and its surroundings.   The more probable state is always one of higher disorder.
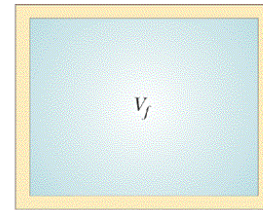
The entropy is a measure of the disorder of a state.
Entropy can be defined using the macroscopic concepts of heat and temperature.

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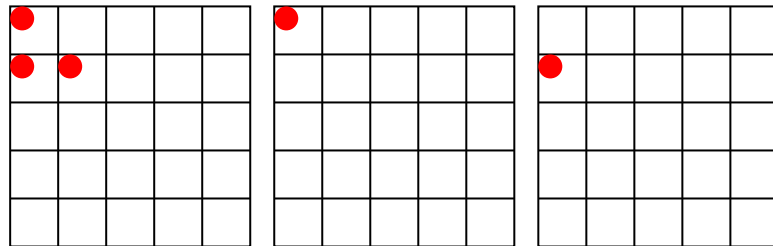
V_t Vacuum

(a)

V_f
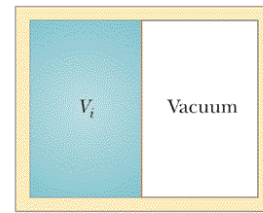
(b)

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The number of possible microstates for N molecules is $W_i = \left(\dfrac{V_i}{V_m}\right)^N$

$$\frac{P_f}{P_i} = \frac{W_f}{W_i} = \frac{\left(\dfrac{V_f}{V_m}\right)^N}{\left(\dfrac{V_i}{V_m}\right)^N} = \left(\frac{V_f}{V_i}\right)^N$$

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

Entropy is a measure of microscopic disorder.