# Lecture# 6

Heat Engines

The fundamental difference between heat and work is the difference in the entropy transfer. Work, being energy transfer by the change of external parameter – such as the position of a piston – does not create any new entropy in system and universe (if done by proper reversible process). All types of work are freely convertible into mechanical work and into each other.

An ideal electrical motor is a device to convert all electrical work into mechanical work, provided there are no mechanical friction or electrical resistance. Work can be completely converted into heat, but inverse is not true.

Entropy enters the system with heat *but does not leave the system with work*. System must have a way to get rid of the entropy.
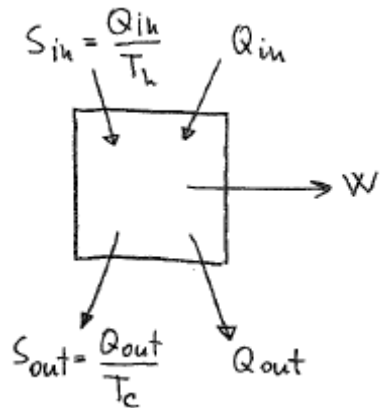
The laws of a cyclic heat engine operation

1) 1st law $Q_{in} = W + Q_{out}$ (That is the best we may get)
ΔU is 0 because it can be only positive (negative means we are getting energy for free). Then if we continuously operate our machine U will go up and it will explode.

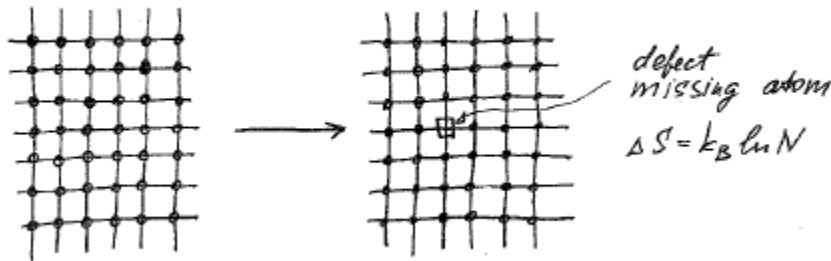2) Entropy has to be removed from the system. The entropy will lead to the explosion of a system.

Example 1
Say our system is ideal gas; the entropy of the system can be expressed as $S(P,V,T,N)$ – but because we have an equation of state $PV = Nk_B T$ only three variables in S are independent, so we have $S(V,T,N)$, if we fix number of molecules and keep T =const. (to keep energy constant) then to accommodate the increase in S system must increase volume. So it will blow out.
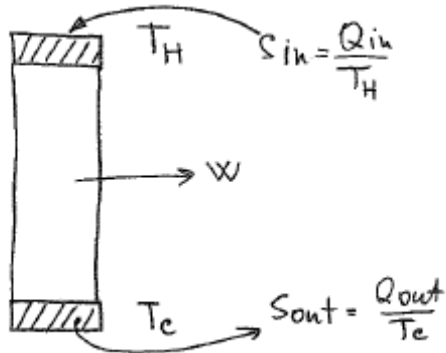
Example 2 Thermoelectric

Voltage can be converted itno work.
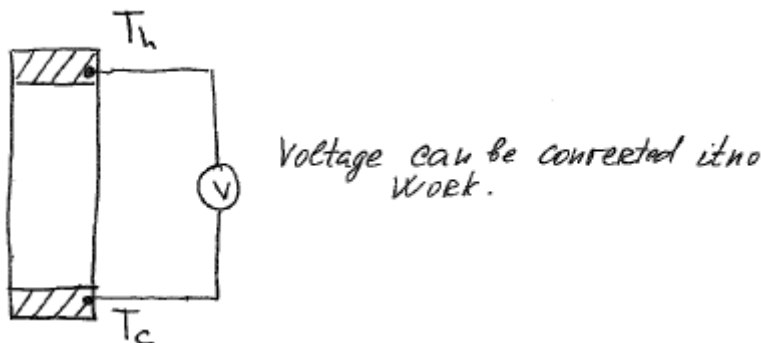
Thermoelectric are crystalline materials and one way to accommodate the entropy is to create point defects.

defect
missing atom

$$\Delta S = k_B \ln N$$

But if we keep pumping entropy into the system, the number of defects will increase and system will "blow out". Conclusion: entropy has to be removed from the system.

T_H $S_{in} = \dfrac{Q_{in}}{T_H}$

W

T_c $S_{out} = \dfrac{Q_{out}}{T_c}$

The best we can do $S_{in} = S_{out}$ (no production of extra entropy; but if we have some friction in the system (resistance of thermoelectric for example) or if we carry process not slow enough we produce some extra entropy that also has to be removed from the system.
$S_{out} = S_{in} + S_{extra}$.

$S_{in} \leq S_{out}$

Idealized heat engine

(1) $\eta = \dfrac{W}{Q_{IN}}$ -efficiency of a heat engine (definition)

(2) $Q_{OUT} = Q_C$ (heat removed from the system by a cold reservoir)

(3) $Q_{IN} = Q_H$ (*hot*) (heat supplied by heater)

(4) $W = Q_H - Q_c$

Combining (1) and (4) we have

(5) $\eta = \dfrac{Q_H - Q_c}{Q_H} = 1 - \dfrac{Q_c}{Q_H}$

On the other hand, $S_H \leq S_C$ and therefore $\dfrac{Q_H}{T_H} \leq \dfrac{Q_C}{T_C}$ and $\dfrac{Q_c}{Q_H} \geq \dfrac{T_c}{T_H}$.

We have than

(6) $\eta \leq 1 - \dfrac{T_C}{T_H}$ - the Carnot inequality

If you want to have absolutely efficient engine then you have two options

1) $T_H \rightarrow \infty$

2) $T_c \rightarrow 0$

2

$\eta = 1 - \dfrac{T_C}{T_H}$ - the Carnot efficiency. It is highest possible efficiency of heat engine.

In power plant steam turbines, which are supposed to operate continuously for years, the upper temperature is currently limited by about 600 K by problems with strength and corrosion of steel. With $T_c = 300k$ and $T_H = 600k$, $\eta = 0.5$. Losses caused by irreversibility's reduce this efficiency to 40%.

Carnot Cycle
The simplest and most known process that produces the Carnot efficiency is the Carnot cycle. In the Carnot cycle a gas or another working substance is expanded and compressed in four stages: two isothermal and two adiabatic (actually isentropic to keep all parameter well defined).

Plot of the Carnot cycle in entropy vs. temperature form.
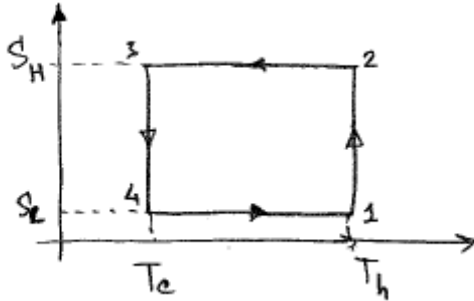
$dU = dQ - dW \qquad dU = TdS - PdV$

$\oint dU = 0 = \oint TdS - \oint PdV$

$\oint TdS = \oint PdV = W$ useful work done by system

$\oint TdS = \int_{S_L}^{S_H} T_H dS + \int_{S_H}^{S_L} T_C dS = T_H (S_H - S_L) + T_L (S_L - S_H) = (T_H - T_L)(S_H - S_L) > 0$
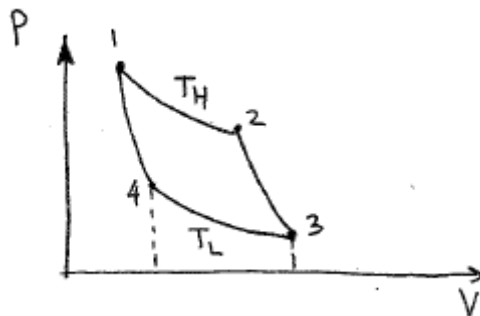
$(T_H - T_L)(S_H - S_L) > 0$ is work done by system, It is positive.

Any process described by figure is called a Carnot cycle regardless of substance
Heat taken by system is

$Q = \int_{S_L}^{S_H} T_H dS = T_H (S_H - S_L)$

Carnot efficiency $\eta = \dfrac{W}{Q_H} = \dfrac{T_H - T_L}{T_H} = 1 - \dfrac{T_L}{T_H}$ - maximum possible value

The Carnot cycle for ideal Monoatomic gas

3

Heat supplied to the engine?

(1->2) Isothermal expansion

$W_S = U_1 - U_2 = Q_H$. Because temperature in the process 1-2 does not change, we have $W_S = Q_H$

$$W_S = \int PdV = RT \int_{V_1}^{V_2} \frac{dV}{V} = RT_H \ln\left(\frac{V_2}{V_1}\right) = Q_H$$

(2->3) Adiabatic expansion

$\Delta Q = 0 \quad W_S = U_2 - U_3 = 3R\ (T_H - T_C)/2$

(3->4)   Isothermal compression, $\Delta U = 0$

$$W_S = \int PdV = RT_C \ln\left(\frac{V_4}{V_3}\right) = Q_C < 0$$

(4->1) Adiabatic compression

$\Delta Q = 0$

$$W_S = U_4 - U_1 = \frac{3}{2}R\left(T_C - T_H\right)$$

Efficiency

$$\eta = \frac{W}{Q_H} = \frac{RT_H \ln\left(\frac{V_2}{V_1}\right) + RT_C \ln\left(\frac{V_4}{V_3}\right)}{RT_H \ln\left(\frac{V_2}{V_1}\right)} = 1 - \frac{T_C}{T_H}$$

This is because $\left(\frac{V_3}{V_4}\right) = \left(\frac{V_2}{V_1}\right)$

Adiabatic process $VT^{\frac{f}{2}} = const$, we have then $\left[\dfrac{V_3}{V_2} = \left(\dfrac{T_H}{T_c}\right)^{\frac{3}{2}} = \dfrac{V_4}{V_1}\right] \Rightarrow \dfrac{V_2}{V_1} = \dfrac{V_4}{V_3}$

Kelvin – Plank formulation of the second Law

It is impossible for any cyclic process to occur whose sole effect is the extraction of heat from reservoir and the performance of an equivalent amount of work.

Why the above formulation is equivalent to our formulation

Reasoning
Let's assume that the above law is wrong
Say we have an ideal engine such that Q = W. Then upon each cycle, we take from some heat reservoir some amount of entropy $\Delta Q/T_H$. This entropy cannot be saved in the system because our engine is cyclic and we return to the same point (with the same system entropy). Therefore our engine (with Q=W) is able to "dissipate" entropy taken from reservoir and as a result total entropy of the universe decreases – which contradict the second law that the entropy stays constant or increases.

Refrigerator is a heat engine operating in reverse, more or less.
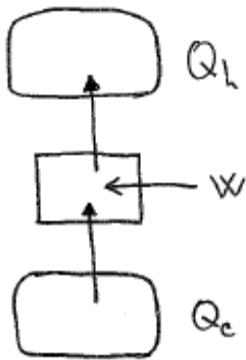
Example
thermoelectric – if you apply voltage difference you create temperature difference.
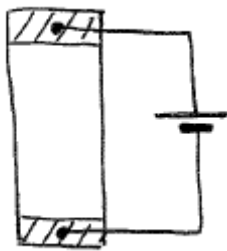
(COP) Coefficient of Performance
COP is a measure of "efficiency" of refrigerator.

$$COP = \frac{Q_c}{W}$$

$$Q_h = W + Q_c \quad \frac{Q_H}{T_H} \geq \frac{Q_c}{T_c} \quad \Rightarrow COP \leq \frac{T_c}{T_H - T_c}$$

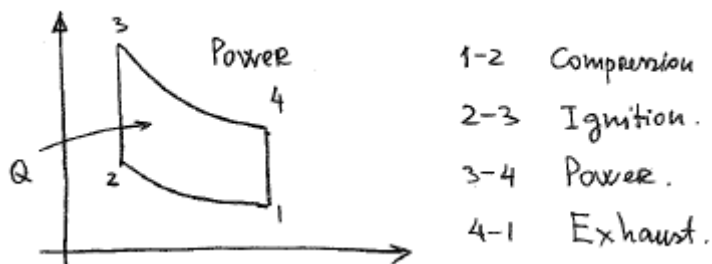Kitchen refrigerator $T_H = 298k$ $T_C = 255k$.
COP = 5.9.
For each joule of energy (electrical) drown from the wall coolant can suck 5.9J of heat from inside refrigerator.

Problem 4.14 heat pump
Problem 4.14 heat conduction of the building.

Real engines,
Internal Combustion Engines
Gasoline engine, Otto cycle

1-2   Compression
2-3   Ignition.
3-4   Power.
4-1   Exhaust.

The engine does not have "hot reservoir" instead the energy is produced internally by burning the fuel. The efficiency of gasoline engine is the net work produced during the cycle divided by "heat" absorbed in ignition step.

(11-1)

$$e = \frac{W}{Q_{23}} \quad Q_{23} = U_3 - U_2 = \frac{f}{2} Nk(T_3 - T_2) = \frac{f}{2}(P_3 V_2 - P_2 V_2)$$

$$W = \oint p \, dV$$

$$W_{34} = \int p \, dV = \int P_3 V_2^r \cdot \frac{1}{V} dV = P_3 V_2^\gamma \cdot \frac{1}{-r+1} V^{-\gamma+1})_{V_2}^{V_1} =$$

$$(34 \, adiabatic \, process, PV^r = const. \, on \, the \, line \, 34 \; P = \frac{1}{V^\gamma} \cdot P_3 V_2^r)$$

$$W_{34} = P_3 V_2^r \cdot \frac{1}{-r+1} \cdot \left[\frac{1}{V_1^{r-1}} - \frac{1}{V_2^{r-1}} \right]$$

$$W_{12} = P_1 V_1^r \cdot \left(\frac{1}{-r+1} \right) \left(\frac{1}{V_2^{r-1}} - \frac{1}{V_1^{r-1}} \right)$$

$P_1 V_1^r = P_2 V_2^r -$ 1 and 2 seat on the same adiabatic

(11-2)

$$W_{34} + W_{12} = \left(P_3 V_2^r - P_2 V_2^\gamma \right) \frac{1}{(\gamma-1)} \left[\frac{-1}{V_1^{r-1}} + \frac{1}{V_2^{r-1}} \right] = \frac{1}{\gamma-1} \left(\frac{-1}{V_1^{r-1}} + \frac{1}{V_2^{r-1}} \right) \cdot V_2^{r-1} \cdot (P_3 V_2 - P_2 V_2)$$

Efficiency $\; e = \dfrac{W}{Q_{23}} = \dfrac{1}{\gamma-1} \cdot \dfrac{2}{f} \cdot \left[1 - \left(\dfrac{V_2}{V_1} \right)^{\gamma-1} \right]$

We take Q_{23} from eq. (11-1)

$$r - 1 = \frac{f+2}{f} - 1 = \frac{2}{f}$$

$$(11-3) \quad e = 1 - \left(\frac{V_2}{V_1} \right)^{\gamma-1}$$

Efficiency depends upon on comparison ratio r = 7/5 typical compression ratios are 8, so

$e = 1 - \left(\dfrac{1}{8} \right)^{2/5} = 0.56$ (really 20 – 30%) using expression for adiabatic $VT^{f/2} = $ const eq (11-3) can be re-written.

$$e = 1 - \left(\frac{V_2}{V_1} \right)^{r-1} = 1 - \frac{T_1}{T_2} = 1 - \frac{T_4}{T_3} \, smaller \, then \, the \, Carnot \, efficiency \, 1 - \frac{T_1}{T_3}$$

The obvious way to improve efficiency is to increase comparison ratio however the fuel mixture becomes too hot and preignite "spontaneously".

One way to avoid "preignition" is to use proper gasoline.

Octane eating characterizes auto ignition resistance of gasoline. Octane measured relative to a mixture of isooctane and n-heptanes at 87-octane gasoline has the same octane rating as a mixture of 87% isooctane and 13-vol % n-heptanes. It does not mean however that the gasoline actually should contain there chemical in this proportion. It simply means it has the same auto ignition resistance as described mixture.
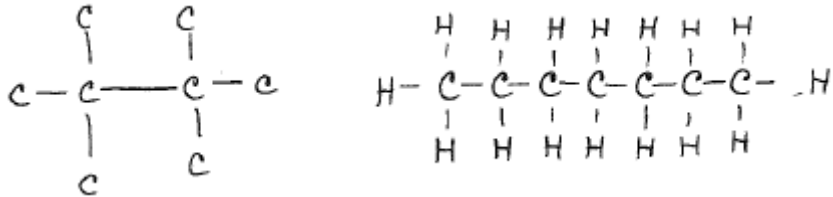
It is interesting that US 8 J gasoline is 91 – 95 in Europe

Misconception: Higher octane rating does not mean better efficiency and better mileage. Ethanol, C_2H_5OH, provides strong auto ignition resistance but does not bring extra energy. (Actually it is a bit lower). You have to by a type of gas that is specified in manual.

Diesel engine

b-c – injection/ ignition
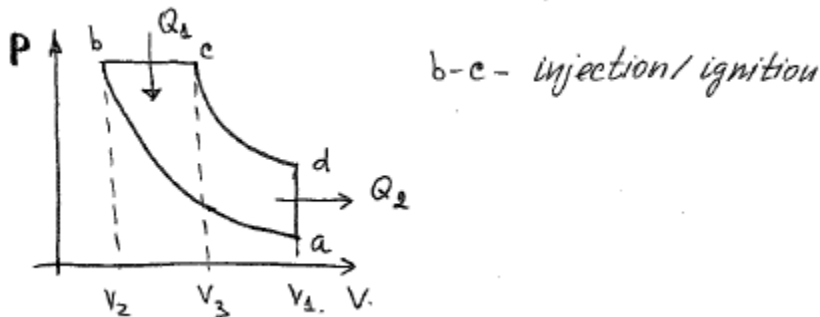
$$\eta = \frac{W}{Q_1}$$

$$W = \oint P dV$$

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

$$\Delta U = 0 \Rightarrow \oint P dV = \oint Q$$

$$\oint P dV = Q_1 + Q_2$$

Adiabatic processes,

$$PV^{\gamma} = const. \quad P_a V_a^{\gamma} = P_b V_b^{\gamma}$$

$$P_d V_d^{\gamma} = P_c V_c^{\gamma} = P_b V_c^{\gamma} \quad (P_b = P_c)$$

$$\frac{P_c}{P_b} = \left(\frac{V_2}{V_1}\right)^{\gamma} \qquad \frac{P_d}{P_b} = \left(\frac{V_3}{V_1}\right)^{\gamma}$$

$$Q_1 = C_p \left(T_c - T_b \right) \qquad Q_2 = C_v \left(T_a - T_d \right)$$

$$\eta = 1 + \frac{Q_2}{Q_1} = 1 + \frac{C_v}{C_p} \frac{T_a - T_d}{T_c - T_b} = 1 + \frac{1}{\gamma} \frac{P_a V_a - PdVd}{P_c V_c - P_b V_b} = 1 + \frac{1}{\gamma} \cdot \frac{V_1 \left(P_a - P_d \right)}{P_b \left(V_3 - V_2 \right)} = 1 + \frac{1}{\gamma} \frac{\left(\dfrac{P_a}{P_b} - \dfrac{P_d}{P_b} \right)}{\left(\dfrac{V_3}{V_1} - \dfrac{V_2}{V_1} \right)} =$$

$$= 1 - \frac{1}{\gamma} \cdot \frac{\left(\dfrac{V_2}{V_1} \right)^{\gamma} - \left(\dfrac{V_3}{V_1} \right)^{\gamma}}{\left(\dfrac{V_2}{V_1} \right) - \left(\dfrac{V_3}{V_1} \right)}$$

In typical diesel compression ratio

$$\frac{V_1}{V_2} \simeq 18$$

Cut off ratio $\dfrac{V_3}{V_2} = 2$

$$\eta = 1 - \frac{5}{1} \cdot \frac{\left(\dfrac{1}{18} \right)^{\frac{1}{5}} - \left(\dfrac{1}{9} \right)^{\frac{1}{5}}}{\left(\dfrac{1}{18} \right) - \left(\dfrac{1}{9} \right)} \simeq 0.65 = 65\%$$

In real diesels the efficiency is about 40 %.