Lecture Notes 7

1. The Gasoline Engine: Otto Cycle

The Otto cycle is a thermodynamic cycle that describes the functioning of a typical spark ignition piston engine. It is the most common cycle for car engines. In 1876 the German engineer Nicolaus Otto built a working four-stroke engine, using gasoline as fuel.

Figure 1: Nicolaus August Otto (1832 – 1891)
was a German engineer who developed the internal combustion engine.

The four steps of the cycle are: 1 to 2 adiabatic compression from v_1 to v_2; 2 to 3 isochoric (at volume v_2) heating; 3 to 4 adiabatic expansion; 4 to 1 isochoric at volume v_1 cooling.

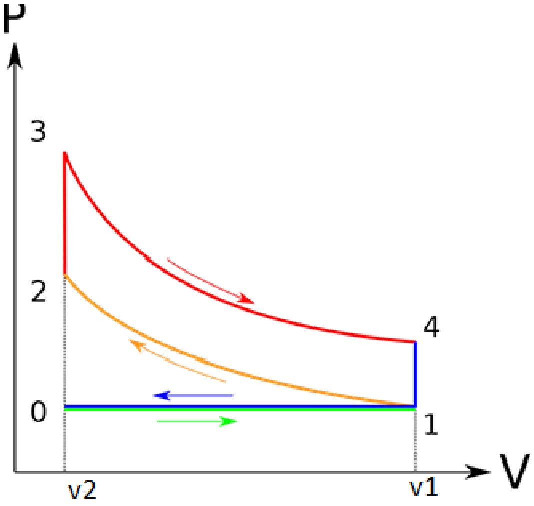


Figure 2: Otto cycle

Step 0–1: a mass of air is isobarically drawn into piston/cylinder arrangement.

Step 1–2: an adiabatic compression of the gas as the piston moves from bottom to top.

Step 2–3: an isochoric heat transfer to the working gas from an external source while the piston is at top. The fuel-air mixture is ignited. The fuel burns rapidly. Through the combustion of fuel, heat is added.

Step 3–4: an adiabatic expansion. This is the power stroke.

Step 4–1: isochoric process in which heat is expelled while the piston is at bottom.

Step 1–0: the mass of air is released to the atmosphere in a isobaric process.

In our simplified analysis we will ignore the 0-1 and 1-0 steps.

We will assume that the working fluid is an ideal van der Waals fluid (see Lecture Notes 5) characterized by:

$$p = \frac{RT}{v-b} - \frac{a}{v^2}, \tag{1}$$

$$u = \frac{i}{2}RT - \frac{a}{v} \tag{2}$$

where u is molar energy and v is molar volume. We next calculate the work done on the gas and the heat added to the gas for each step.

1 to 2. Adiabatic Compression

$$Q_{12} = 0 \tag{3}$$

$$\Delta U_{12} = N\frac{i}{2}R(T_2 - T_1) - Na(\frac{1}{v_2} - \frac{1}{v_1}) \tag{4}$$

We get the heat by using the 1st Law:

$$W_{12} = \Delta U_{12} - Q_{12} = N\frac{i}{2}R(T_2 - T_1) - Na(\frac{1}{v_2} - \frac{1}{v_1}) \tag{5}$$

2 to 3. Isochore v = v_2; Ignition and burning of fuel. This is the heating step.

$$W_{23} = 0 \tag{6}$$

$$\Delta U_{23} = N\frac{i}{2}R(T_3 - T_2) \tag{7}$$

We get the heat by using the 1st Law:

$$Q_{23} = \Delta U_{23} - W_{23} = N\frac{i}{2}R(T_3 - T_2) \tag{8}$$

3 to 4. Adiabatic Expansion. Power stroke.

$$Q_{34} = 0 \tag{9}$$

$$\Delta U_{34} = N\frac{i}{2}R(T_4 - T_3) - Na(\frac{1}{v_1} - \frac{1}{v_2}) \tag{10}$$

We get the heat by using the 1st Law:

$$W_{34} = \Delta U_{34} - Q_{34} = N\frac{i}{2}R(T_4 - T_3) - Na(\frac{1}{v_1} - \frac{1}{v_2}) \qquad (11)$$

4 to 1. Isochore v = v_1

$$W_{41} = 0 \qquad (12)$$

$$\Delta U_{41} = N\frac{i}{2}R(T_1 - T_4) \qquad (13)$$

We get the heat by using the 1st Law:

$$Q_{41} = \Delta U_{41} - W_{41} = N\frac{i}{2}R(T_1 - T_4) \qquad (14)$$

The total work done on the gas is: $W_{tot} = W_{12} + W_{23} + W_{34} + W_{41}$. We find by using equations: (5), (6), (11), (12):

$$W_{tot} = -N\frac{i}{2}R(T_1 - T_2 + T_3 - T_4)$$

Hence the total work done by the gas is:

$$-W_{tot} = N\frac{i}{2}R(T_1 - T_2 + T_3 - T_4) \qquad (15)$$

The efficiency e of the engine is the ratio of the output work $-W_{tot}$ to the input heat Q_{23}. Using equations (11) and (15) we find:

$$e = \frac{-W_{tot}}{Q_{23}} = 1 - \frac{T_4 - T_1}{T_3 - T_2} \qquad (16)$$

In Lecture Notes 5, Eq. (19), we derived the relation between v and T along an adiabat. We use it for the 1-2 and 3-4 adiabatic steps.

$$(v_2 - b)^{\frac{2}{i}}T_2 = (v_1 - b)^{\frac{2}{i}}T_1 \qquad (17)$$

$$(v_2 - b)^{\frac{2}{i}}T_3 = (v_1 - b)^{\frac{2}{i}}T_4 \qquad (18)$$

Subtract (17) from (18):

$$(v_2 - b)^{\frac{2}{i}}(T_3 - T_2) = (v_1 - b)^{\frac{2}{i}}(T_4 - T_1) \qquad (19)$$

Or

$$\frac{T_4 - T_1}{T_3 - T_2} = (\frac{v_2 - b}{v_1 - b})^{\gamma - 1} \qquad (20)$$

where $\gamma - 1 = 2/i$.

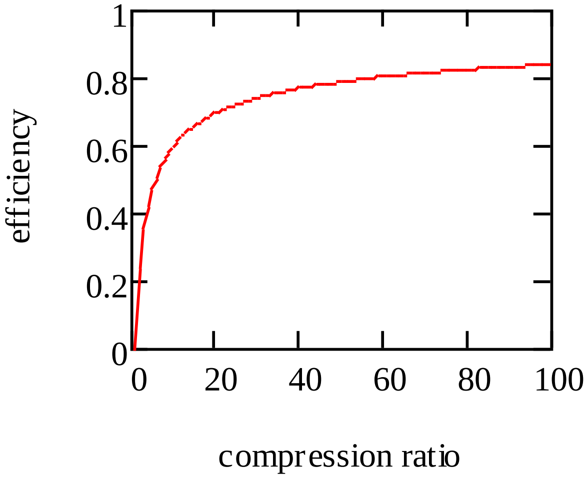
The efficiency is obtained from Eqs. (16) and (20):

$$e = 1 - (\frac{v_2 - b}{v_1 - b})^{\gamma - 1} \qquad (21)$$

In Computer Lab 4 we studied the Otto cycle assuming the thermodynamic system to be an ideal gas. Then we set b = 0 in Eq. (21) and get:

$$e = 1 - (\frac{v_2}{v_1})^{\gamma-1} = 1 - r^{-(\gamma-1)} \qquad (22)$$

where r = v_1/v_2 is the compression ratio.



<u>Readings</u>
Computer Lab 5.
Callen Ch. 4, Sec. 10; Pr. 4.10.2
HRW Ch. 20; Pr. 20.35
Problem Sets 9.

Lecture Notes 8

1. Second Law of Thermodynamics

The British physicist Arthur Eddington wrote in 1915 to his colleagues: “If your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation”. This expresses the confidence physicists have in this law.

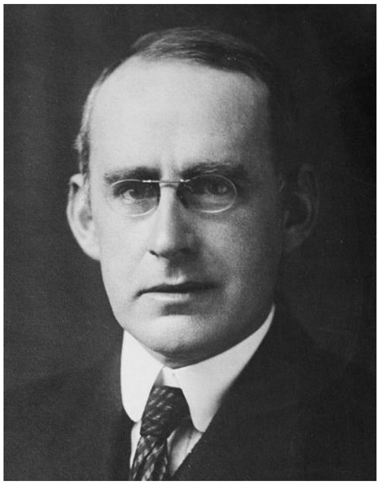


Figure 1: Arthur Eddington (1882–1944), British physicist, astronomer

The second law has several equivalent formulations. We will start with the one in Callen’s textbook, postulate 2 in chapter 1.

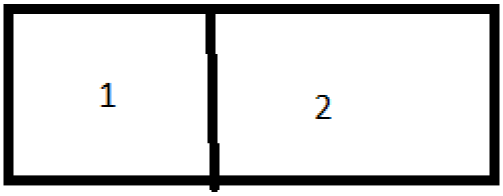
The values assumed by the extensive parameters in the absence of an internal constraint maximize the entropy over the constrained equilibrium states.

We have seen an example of this in computer lab #0. There we studied the equilibrium of a hot object and a cold object. The system was constrained: its total energy was fixed. We released an internal constraint by allowing heat to be exchanged between the two objects. We have seen that entropy is maximized when the temperatures are equal, which we know empirically is what it happens.

We next prove that the uniformity of intensive thermodynamic quantities is demanded by the entropy maximization. In what follows I will write the 1st law as follows:

$$dS = (1/T)dU + (p/T)dV - (\mu/T)dN \qquad (1)$$

I Thermal Equilibrium



The two objects have energies U_1 and U_2 respectively. Initially all walls are rigid and adiabatic. We remove the insulation on the internal wall making it diathermal. As a result, heat is exchanged. We keep the external constraint that the total energy is fixed.

$$U_1 + U_2 = U \qquad (2)$$

The entropy is additive. Hence:

$$S = S_1(U_1) + S_2(U_2) = S_1(U_1) + S_2(U-U_1) \qquad (3)$$

We maximize S by setting the derivative of the entropy with respect to energy of object 1 equal to zero.

$$\left(\frac{\partial S}{\partial U_1}\right)_{V,N} = \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1,N_1} - \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2,N_2} = 0 \qquad (4)$$

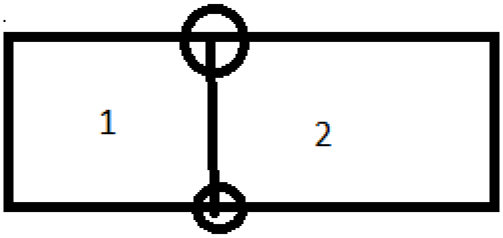
Hence, in view of Eq. (1):

$$1/T_1 = 1/T_2, \text{ or } T_1 = T_2. \qquad (5)$$

Thus thermal equilibrium is achieved when temperature is uniform as demanded by the second law of thermodynamics.

II. Thermo-mechanical equilibrium

Initially all walls are adiabatic and rigid. Then we released constrains by making the internal wall mobile and diathermal.



We keep the constrains that the total energy and the total volume are constants.

$$U_1 + U_2 = U \tag{6}$$

$$V_1 + V_2 = V \tag{7}$$

The entropy is additive:

$$S = S_1(U_1, V_1) + S_2(U_2, V_2) = S_1(U_1, V_1) + S_2(U-U_1, V-V_1) \tag{8}$$

We now maximize S by setting the derivatives of entropy with respect to energy and volume equal to zero.

$$\left(\frac{\partial S}{\partial U_1}\right)_{V_1,N_1} = \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1,N_1} - \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2,N_2} = 0 \tag{9}$$

$$\left(\frac{\partial S}{\partial V_1}\right)_{U_1,N_1} = \left(\frac{\partial S_1}{\partial V_1}\right)_{U_1,N_1} - \left(\frac{\partial S_2}{\partial V_2}\right)_{U_2,N_2} = 0 \tag{10}$$

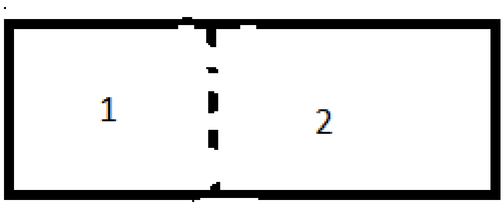
Hence, in view of equation 1:

$$1/T_1 = 1/T_2 \text{ or } T_1 = T_2 \tag{11}$$

$$p_1/T_1 = p_2/T_2 \text{ or } p_1 = p_2 \tag{12}$$

Thus thermal and mechanical equilibrium is achieved when temperature and pressure are uniform as demanded by the second law of thermodynamics.

III Thermal and Matter Flow Equilibrium



Initially all walls are adiabatic and impermeable. Then we release constrains by making the internal wall permeable and diathermal. We keep the constrains that the total energy and the total number of moles are constants.

$U_1 + U_2 = U$ (13)

$N_1 + N_2 = N$ (14)

The entropy is additive:

$S = S_1(U_1, N_1) + S_2(U_2, N_2) = S_1(U_1, N_1) + S_2(U-U_1, N-N_1)$ (15)

We now maximize S by setting the derivatives of entropy with respect to energy and number of moles equal to zero.

$$\left(\frac{\partial S}{\partial U_1}\right)_{V_1,N_1} = \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1,N_1} - \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2,N_2} = 0 \qquad (16)$$

$$\left(\frac{\partial S}{\partial N_1}\right)_{U_1,V_1} = \left(\frac{\partial S_1}{\partial N_1}\right)_{U_1,V_1} - \left(\frac{\partial S_2}{\partial N_2}\right)_{U_2,V_2} = 0 \qquad (17)$$

Hence, in view of equation 1:

$1/T_1 = 1/T_2$ or $T_1 = T_2$ (18)

$\mu_1/T_1 = \mu_2/T_2$ or $\mu_1 = \mu_2$ (19)

Thus thermal and matter flow equilibrium is achieved when temperature and chemical potential are uniform as demanded by the second law of thermodynamics.

<u>Reading</u>

HRW Ch.20
Callen Ch. 1, Sec. 10; Ch. 2, Sec. 4, 6, 7, 8
Problem Set 7, 8

Lecture Notes 9

Second Law of Thermodynamics: Heat Engine, Refrigerator, Air Conditioner, Heat Pump

1. Heat Engine

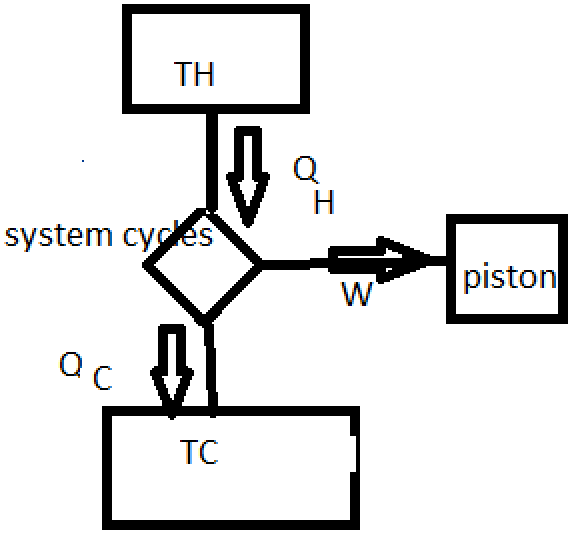


Figure 1: Heat Engine

In a heat engine heat Q_H produced in a heat reservoir (boiler) is transformed by a thermodynamic system (gas, liquid) into work W done on pistons. Q_C (waste heat) is discarded in the cold reservoir (environment). The two reservoirs are large systems (i.e. large heat capacities), so that they process heat isothermally at T_H and T_C, respectively.

$Q_H = -T_H \Delta S_H$ (1)

$Q_C = T_C \Delta S_C$ (2)

ΔS_H is the change in the entropy of the hot reservoir, and ΔS_C is the change in the entropy of cold reservoir The thermodynamic system acts on a cycle. Hence the state variables, energy and entropy, do not change:

$\Delta U = 0$ (3)

and

$\Delta S = 0.$ (4)

The first law of thermodynamics gives: $0 = \Delta U = -W + Q_H - Q_C$. Hence:

$$Q_H = W + Q_C \qquad (5)$$

The total entropy is the sum of hot reservoir entropy S_H, system entropy S and cold reservoir entropy S_C. The change in the total entropy must be positive as dictated by the second law.

$$0 \le \Delta S_{tot} = \Delta S_H + \Delta S + \Delta S_C \qquad (6)$$

Since $\Delta S = 0$

$$0 \le -\frac{Q_H}{T_H} + \frac{Q_C}{T_C} \qquad (7)$$

Substitute Q_C from Eq. (5) into the right hand side of (7):

$$\frac{Q_H}{T_H} \le \frac{Q_H - W}{T_C} \qquad (8)$$

Inequality (8) can be written using the efficiency definition $e = W/Q_H$:

$$e = \frac{W}{Q_H} \le 1 - \frac{T_C}{T_H} \qquad (9)$$

Hence the best efficiency one can hope to achieve with a heat engine acting between two reservoir temperatures is $1-T_C/T_H$. This is called the Carnot efficiency.

Figure 2: Nicolas Leonard Sadi Carnot (1796-1832), French engineer and physicist, father of thermodynamics

A statement equivalent to the 2nd law is due to Kelvin and Planck. It is impossible to design an engine that transforms heat Q_H completely into work W.

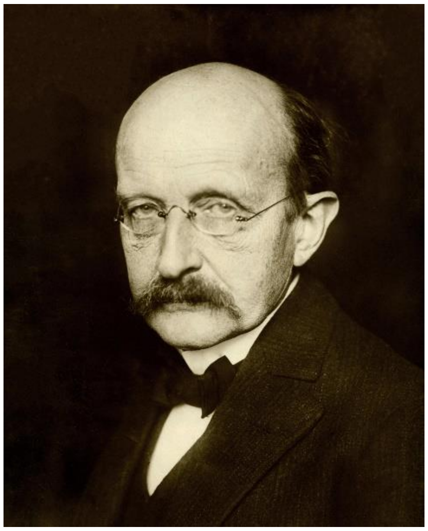


Figure 3: Max Planck (1858-1947), German physicist, father of quantum mechanics

The engine is supposed to work on cycles: $\Delta S = 0$.

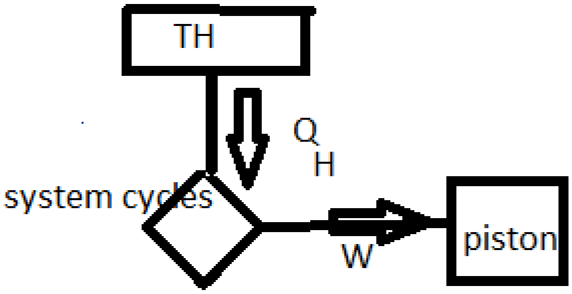


Figure 4: Impossible Heat Engine

For this hypothetical engine: $\Delta S_{tot} = \Delta S_H + \Delta S = -Q_H/T_H < 0$. This is forbidden by the 2nd law.

2. Refrigerator

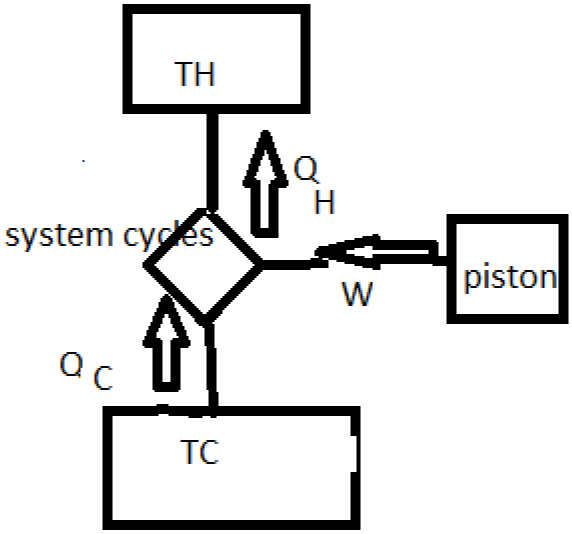


Figure 5: Refrigerator

A refrigerator uses work W (electric system) to extract heat Q_C from the cold reservoir (freezer) and discard waste heat Q_H into the hot reservoir (kitchen). The thermodynamic system (Freon, ammonia NH3) acts on cycles. Hence ΔU = ΔS = 0. The first law gives: 0 = ΔU = W - Q_H + Q_C, which we write as:

$$Q_H = W + Q_C \tag{10}$$

The second law is:

$$0 \le \Delta S_{tot} = \Delta S_H + \Delta S + \Delta S_C \tag{11}$$

with ΔS = 0. The reservoirs act isothermally:

$$Q_H = T_H \Delta S_H \tag{12}$$

$$Q_C = -T_C \Delta S_C \tag{13}$$

Using (11), (12), (13) we get:

$$0 \le \frac{Q_H}{T_H} - \frac{Q_C}{T_C} \tag{14}$$

Substitute Q_H from (10) into (14):

$$\frac{Q_C}{T_C} \le \frac{Q_C + W}{T_H} \tag{15}$$

We define the coefficient of performance (COP) as ratio of output (Q_C) to input (W). Using (15) we get:

$$COP = \frac{Q_C}{W} \leq \frac{T_C}{T_H - T_C} \qquad (16)$$

The maximum possible COP is called the Carnot COP. A statement equivalent to the 2nd law is due to Clausius. It is impossible to design a refrigerator that transfers heat Q from a cold reservoir T_C to a hot reservoir T_H without expending any work W.

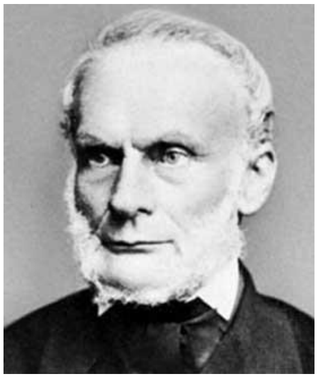


Figure 6: Rudolph Clausius (1822-1888), German physicist, founder of thermodynamics.

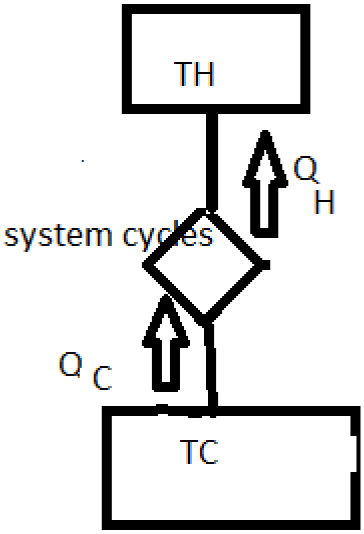


Figure 7: Impossible Refrigerator

Since W = 0 the 1'st law gives $Q_H = Q_C = Q$. The total entropy change is:

$$\Delta S_{tot} = \Delta S_H + \Delta S + \Delta S_C = -\frac{Q}{T_C} + \frac{Q}{T_H} < 0 \qquad (17)$$

To get (17) I used $\Delta S = 0$, since we consider the system works in cycles. The last inequality follows from $T_H > T_C > 0$, $Q > 0$. Inequality (17) contradicts the law of entropy (2'nd law). Hence such a refrigerator cannot be built.

3. Air Conditioner

The air conditioner is used in the summer to transfer heat from inside of the house (cold reservoir) to outside of house (hot reservoir). It has the same scheme as the refrigerator, Figure 4. Its COP is defined as output (Q_C) divided by input (W) satisfies:

$$COP = \frac{Q_C}{W} \leq \frac{T_C}{T_H - T_C} \qquad (18)$$

4. Heat Pump

Heat pump is used in the winter to transfer heat from a cold place (outside of house) to a hot place (inside of house). It has the same scheme as the refrigerator, Fig.4. Its coefficient of performance is ratio of output (heat introduced in hot place) to input (work).

$$COP = \frac{Q_H}{W} \leq \frac{T_H}{T_H - T_C} \qquad (18)$$

5. Carnot Cycle

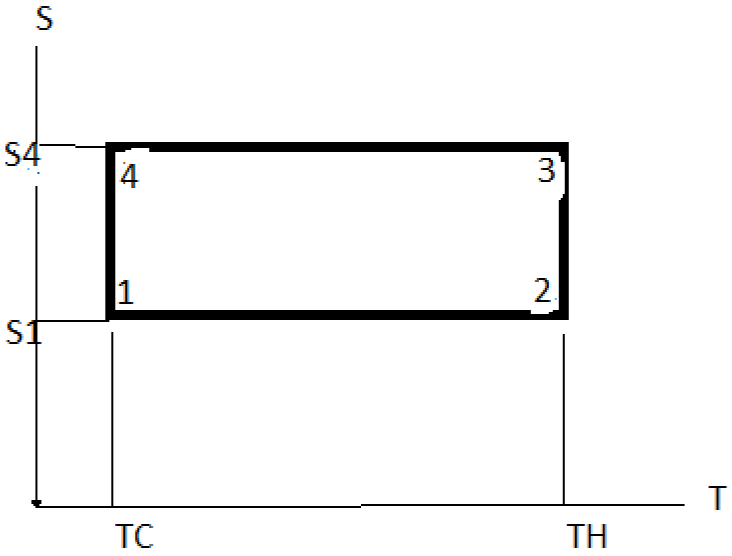


Figure 8: Carnot cycle

The engine Carnot cycle contains two adiabats and two isotherms at temperatures T_C and T_H, respectively. We will next evaluate its efficiency.

On adiabat 1 to 2: $Q_{12} = 0$.

On isotherm 2 to 3: $Q_{23} = T_H(S_4 - S_1)$. This is the heating step.

On adiabat 3 to 4: $Q_{34} = 0$.

On isotherm 4 to 1: $Q_{41} = T_C(S_1 – S_4)$.

The total heat received by the system during the cycle is:

$Q = 0 + T_H(S_4 - S_1) + 0 + T_C(S_1 – S_4) = (T_H - T_C)(S_4 - S_1)$. (19)

Using the 1’st law for the cycle, we calculate the work: $0 =\Delta U = W + Q$. Hence the work done on pistons during a cycle is: $-W = Q = (T_H - T_C)(S_4 - S_1)$. The efficiency is:

$e = -W/Q_{23}= 1 - T_C/T_H$ (20)

We have proved above, Eq. (9), that this efficiency is the highest that the laws of thermodynamics allow an engine working on cycles to achieve. Moreover, the Carnot cycle efficiency holds for no matter what thermodynamic system.

<u>Reading</u>
HRW Ch.20
Callen Ch. 4
Problem Set 9