

Title:Carnot Theorem

Course:B.Sc part 2 chemistry (Hons.)

By, Sanjeev Kumar Gautam

Department of chemistry

S.S College Jehanabad

1 Equivalence of Kelvin and Clausius formulations

Last time we learned that the Second Law can be formulated in two ways.

The Kelvin formulation:

No process is possible whose sole result is the complete conversion of heat into work.

It can be also expressed in a slightly different form: *It is impossible to transform heat systematically into mechanical work in a cycle involving only one bath*

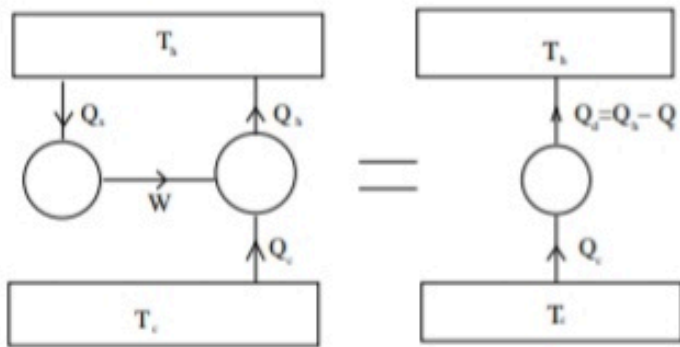
The Clausius formulation:

No process is possible whose sole effect is transfer of heat from a colder to a hotter body.

It was mentioned that these two formulations are equivalent, which can be formally proved as follows.

Suppose the Second Law in the Kelvin's formulation does not hold, i.e. one can produce some work W using only one bath of some temperature T_1 . This work can be transformed into heat, for example by friction. So using the work which the engine produces one can increase the temperature of any other system of arbitrary temperature T_2 . Since T_2 may be higher than T_1 it turns that one transfers heat from colder system to the hot one, which is violation of the Second Law in the Clausius formulation. For instance, one can use the work W to run another engine which operates the inverse Carnot cycle (see the figure below). This combined machine produces no work and its net effect is transferring heat from cold bath to the hot one.

The combined machine absorbs positive heat Q_c from the cold bath, and delivers the heat $Q_d = Q_h - Q_x$ to the hot bath. Clearly, $Q_d > 0$ because $Q_x = W = Q_h - Q_c$. (Note: in this lecture we use symbols Q , W , etc. for absolute values of corresponding quantities.)



Let us made the opposite assumption, i.e. that, in violation of the Clausius formulation, one manages to transfer a certain amount of heat Q from cold bath to the hot one. Suppose it is exactly the heat another heat engine absorbs from the hot bath during isothermal expansion. Then the hot bath receives and gives up the same amount of heat, and remains virtually unchanged. As a result, the net effect is producing work at the expense of heat extracted from a single (cold) bath, which is a violation of the Second Law in the Kelvin formulation.

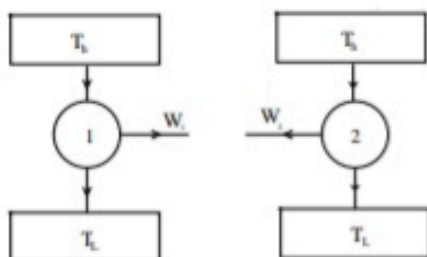
The above argument prove that the Clausius and Kelvin statements are equivalent.

2 First Carnot theorem: General proof

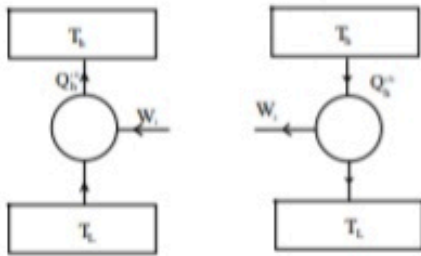
When we considered the Carnot cycle for an ideal gas we have found that efficiency of the cycle $\eta = (T_h - T_c)/T_h$ depends only on temp. of two heat baths and does not depend of gas characteristics, say gas heat capacity. This suggests that the result is actually general and valid for arbitrary gas.

The first Carnot theorem: all reversible engines operating between the same two baths has the same efficiency $\eta = (T_h - T_c)/T_h$.

Consider two Carnot cycle engines using different gases but working between the same two temperatures. Suppose the engines have different efficiencies η_1 and η_2 . The Carnot theorem states that it is impossible. Let us assume for a moment that the theorem is wrong and that efficiencies are different, say $\eta_1 < \eta_2$.



One can demonstrate that this assumption leads to a contradiction. Let us operate the first engine counterclockwise.



This would require some external work. We can use the work produced by the second engine to feed the first one. The reasoning is especially simple for the **special case when** $W_1 = W_2$. Since $\eta = W/Q_h$ the assumption $\eta_1 < \eta_2$ gives

$$Q_h^1 > Q_h^2.$$

Also, recall that

$$\eta = W/Q_h = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}.$$

Then inequalities $\eta_1 < \eta_2$ and $Q_h^1 > Q_h^2$ gives

$$Q_c^1 > Q_c^2.$$

The total heat received from the cold bath is

$$Q_c = Q_c^1 - Q_c^2 > 0$$

and the heat obtained by the hot bath is

$$Q_h^1 - Q_h^2 > 0.$$

The total work produced by the combined engine is zero, and the net result is that some amount of heat is pumped out of cold bath and is given up to the hot bath which is violation of the Second law (in the Clausius formulation).

In general $W_1 \neq W_2$. But one can easily bypass this difficulty in a following way. Suppose W_2/W_1 is a rational number and therefore can be written as $W_2/W_1 = n_1/n_2$ where n_i some integers. Then

$$n_1 W_1 = n_2 W_2.$$

It is important to understand that there is no need to run both machine simultaneously. In the combined machine the first and second engine may work in a sequence. For example, first the second engine performs n_2 cycles and does work $n_2 W_2$, for example lifting the piston. Then the

potential energy of the piston, which is exactly $n_2 W_2$, is spent on running the first engine. If n_1 and n_2 satisfy the condition $n_1 W_1 = n_2 W_2$, then the first engine will performed exactly n_1 cycles.

Let us consider all quantities related to the first engine, such as Q_h^1, Q_c^1, W_1 during not one but n_1 cycles:

$$\tilde{Q}_h^1 = n_1 Q_h^1, \quad \tilde{Q}_c^1 = n_1 Q_c^1, \quad \tilde{W}_1 = n_1 W_1,$$

and similar for the second engine

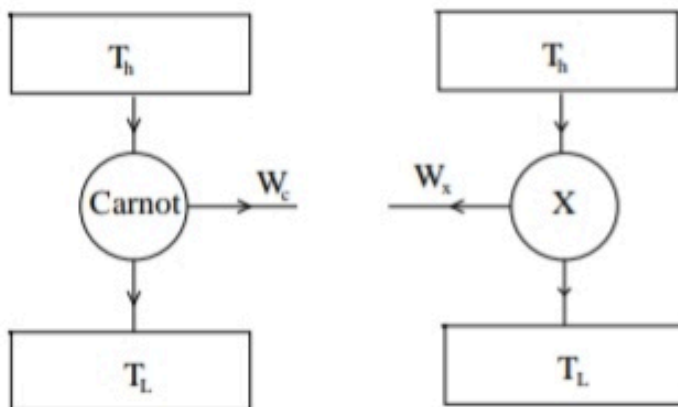
$$\tilde{Q}_h^2 = n_2 Q_h^2, \quad \tilde{Q}_c^2 = n_2 Q_c^2, \quad \tilde{W}_2 = n_2 W_2.$$

Since $\tilde{W}_1 = \tilde{W}_2$, one can repeat the above proof for the case $W_1 = W_2$ just changing the notations, and using the quantities related not to one cycle but to n_1 cycle for the first engine and n_2 cycles for the second one.

3 Second Carnot theorem

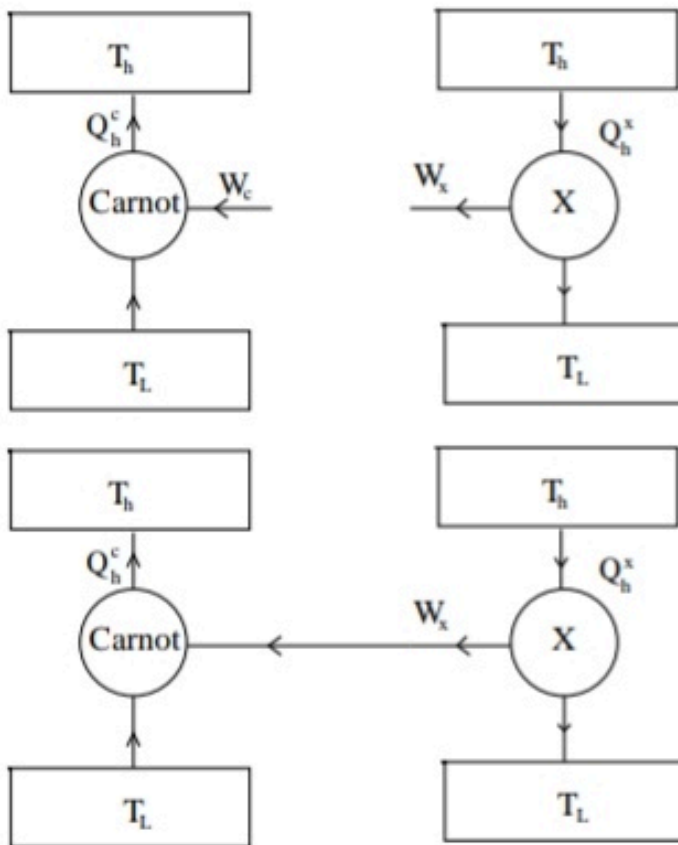
The Carnot cycle is the only reversible cycle which involve only two temperatures. But there are many irreversible cycles operating between two temperatures. If one changes TD parameters of the system fast, say by a sudden move of the piston, evolution of the gas becomes essentially irreversible involving many complicated irreversible processes such as sound propagation.

Consider the Carnot cycle and some other irreversible cycle, both operating between the same two temperatures.



The Second Carnot theorem states that $\eta_c \geq \eta_x$.

Let us assume for a moment that the theorem wrong and that $\eta_c < \eta_x$. One can apply the same trick as before, reversing the Carnot cycle. Considering the combination of two machines



and using the same argument as before, one can see that our assumption $\eta_c < \eta_x$ is inconsistent with the Second Law, and therefore is wrong.

Note: One can ask what prevent us from applying the argument in opposite direction, that is inverting not the Carnot engine but the other machine? But the X machine can not be reversed by definition because its operation involves fast irreversible processes leading to dissipation of energy.

The first and second Carnot's theorems can be formulated together as follows

If there are several heat engines operating between the same two temperatures, then all reversible engines have the same efficiency, while irreversible ones have efficiencies which can never exceed the efficiency of the reversible engines

This theorem is of paramount importance and has implications which go far beyond the area of heat engines.