SECOND LAW OF THERMODYNAMICS, CARNOT CYCLE & ITS EFFICIENCY, CARNOT THEOREM

Paper: Physical Chemistry

(UNIT-II Thermodynamics)

For the students of BSc II

By

Dr Lokesh Kumar Agarwal
Assistant Professor
Department of Chemistry
Mohanlal Sukhadia University, Udaipur

Table of Contents

1. **Learning Outcomes**
2. **Limitations of First law of Thermodynamics**
3. **Second law of Thermodynamics**
4. **Carnot Cycle & its Efficiency**
5. **Carnot Theorem**
6. **Summary**

1. Learning Outcomes

After studying this module you shall be able to:

- Limitations of the first law of thermodynamics
- Various statements of the Second law of thermodynamics
- Know about Carnot Cycle and its efficiency
- Brief knowledge about Carnot Theorem

2. Limitations of the first law of thermodynamics / Why SLOT was needed:

1. **No restriction on the direction of the flow of heat**: the first law establishes definite relationship between the heat absorbed and the work performed by a system. The first law does not indicate whether heat can flow from a cold end to a hot end or not. For example: we cannot extract heat from the ice by cooling it to a low temperature. Some external work has to be done.

2. **Does not specify the feasibility of the reaction**: first law does not specify that process is feasible or not for example: when a rod is heated at one end then equilibrium has to be obtained which is possible only by some expenditure of energy.

3. Practically it is **not possible to convert the heat energy into an equivalent amount of work**. First law does not contradict the existence of heat engine of 100% efficiency or self acting machine. But We can say that such heat engine or machines are not attainable in actual practice

To overcome this limitations, another law is needed which is known as second law of thermodynamics. The second law of thermodynamics helps us to predict whether the reaction is feasible or not and also tell the direction of the flow of heat. It also tells that energy cannot be completely converted into equivalent work.

3. The Second Law of thermodynamics

- Nicolas Léonard Sadi Carnot was a French physicist, who is considered to be the "**father of thermodynamics**," for he is responsible for the origins of the Second Law of Thermodynamics, as well as various other concepts. The current form of the second law uses entropy rather than caloric, which is what Sadi Carnot used to describe the law. Caloric relates to heat and Sadi Carnot came to realize that some caloric is always lost in the motion cycle. Thus, the thermodynamic reversibility concept was proven wrong, proving that irreversibility is the result of every system involving work.
- William Thompson, also known as Lord Kelvin, formulated the Kelvin statement, which states "It is **impossible** to convert heat completely in a cyclic process." This means that there is no way for one to convert all the energy of a system into work, without losing energy. Another statement by Kelvin was formulated: "**No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work**."

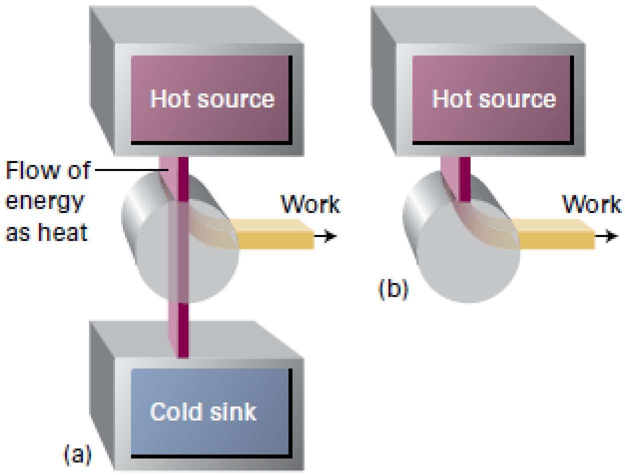


Figure (a) A heat engine is a device in which energy is extracted from a hot reservoir (the hot source) as heat and then some of that energy is converted into work and the rest discarded into a cold reservoir (the cold sink) as heat. (b) The Kelvin statement of the Second Law denies the possibility of the process illustrated here, in which heat is changed completely into work, there being no other change.

- Rudolf Clausius was a German physicist, and he developed another statement of the Second Law which says "**Heat does not flow spontaneously from a cool body to a hotter body**." Or "Heat generally **cannot flow spontaneously** from a material at a lower temperature to a material at a higher temperature."

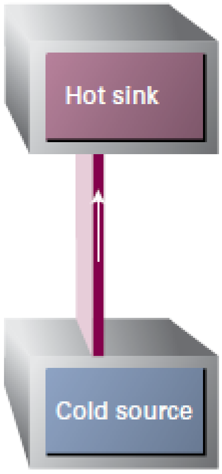


Figure According to the Clausius statement of the Second Law, the process shown here, in which energy as heat migrates from a cool source to a hot sink, does not take place spontaneously. The process is not in conflict with the First Law because energy is conserved.

The Second Law of Thermodynamics also states that entropy of the entire universe, as an isolated system, will always increase over time. The second law also states that the changes in the entropy in the universe can never be negative. It is vitally important when considering applications of the Second Law to remember that it is a statement about the total entropy of the overall isolated system (the 'universe'), not just about the entropy of the system of interest.

The entropy of an isolated system increases in the course of a spontaneous change: $\Delta S_{tot} > 0$.

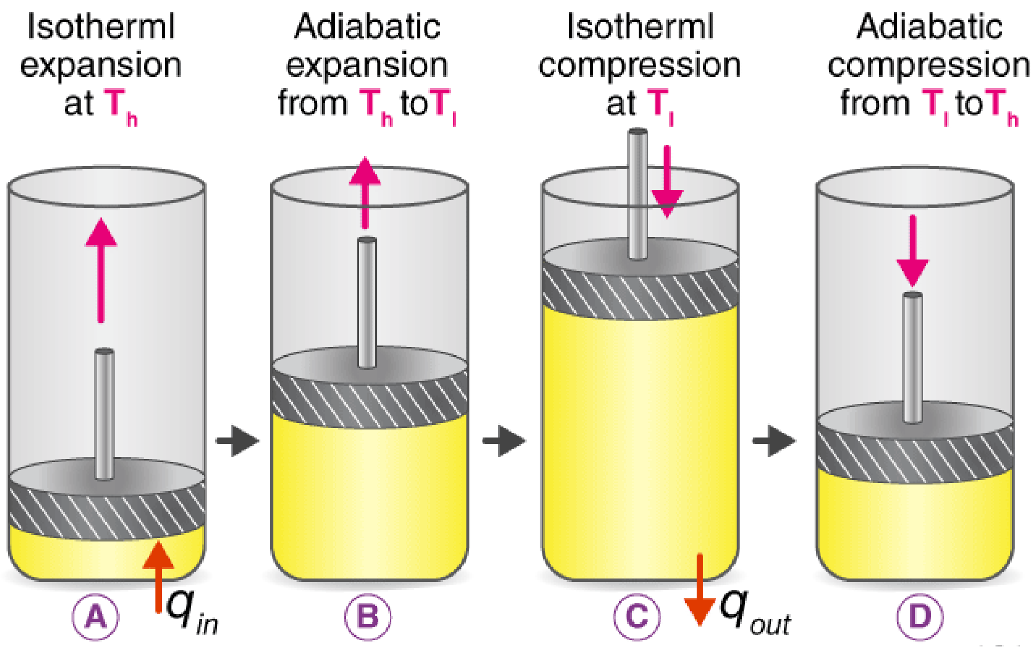
where S_{tot} is the total entropy of the overall isolated system. That is, if S is the entropy of the system of interest, and S_{sur} the entropy of the surroundings, then

$$S_{tot} = S + S_{sur}$$

In summary, the First Law uses the internal energy to identify *permissible* changes; the Second Law uses the entropy to identify which of these permissible changes are *spontaneous*.

4. Carnot Cycle & its Efficiency:

A Carnot cycle is defined as an ideal reversible closed thermodynamic cycle in which there are four successive operations involved, which are isothermal expansion, adiabatic expansion, isothermal compression and adiabatic compression. During these operations, the expansion and compression of substance can be done up to the desired point and back to the initial state.



Following are the four processes of the Carnot cycle:

- In (a), the process is reversible isothermal gas expansion. In this process, the amount of heat absorbed by the ideal gas is q_{in} from the heat source, which is at a temperature of T_h. The gas expands and does work on the surroundings.
- In (b), the process is reversible adiabatic gas expansion. Here, the system is thermally insulated, and the gas continues to expand and work is done on the surroundings. Now the temperature is lower, T_l.
- In (c), the process is reversible isothermal gas compression process. Here, the heat loss q_{out} occurs when the surroundings do the work at temperature T_l.

- In (d), the process is reversible adiabatic gas compression. Again the system is thermally insulated. The temperature again rises back to T_h as the surrounding continue to do their work on the gas.

Steps involved in a Carnot Cycle

For an ideal gas operating inside a Carnot cycle, the following are the steps involved:

Step 1:

Isothermal expansion: The gas is taken from P_1, V_1, T_1 to P_2, V_2, T_2. Heat Q_1 is absorbed from the reservoir at temperature T_1. Since the expansion is isothermal, the total change in internal energy is zero, and the heat absorbed by the gas is equal to the work done by the gas on the environment, which is given as:

$$W_{1\to2} = Q1 = \mu \times R \times T_1 \times ln\frac{v2}{v1} \qquad ...(1)$$

Step 2:

Adiabatic expansion: The gas expands adiabatically from P_2, V_2, T_1 to P_3, V_3, T_2.

Here, work done by the gas is given by:

$$W_{2\to3} = \frac{\mu R}{\gamma-1}(T1 - T2) \qquad ...(2)$$

Step 3:

Isothermal compression: The gas is compressed isothermally from the state (P_3, V_3, T_2) to (P_4, V_4, T_2).

Here, the work done on the gas by the environment is given by:

$$W_{3\to4} = \mu R T_2 \, ln\frac{v3}{v4} \qquad ...(3)$$

Step 4:

Adiabatic compression: The gas is compressed adiabatically from the state (P_4, V_4, T_2) to (P_1, V_1, T_1).

Here, the work done on the gas by the environment is given by:

$$W_{4\to1} = \frac{\mu R}{\gamma-1}(T1 - T2) \qquad ...(4)$$

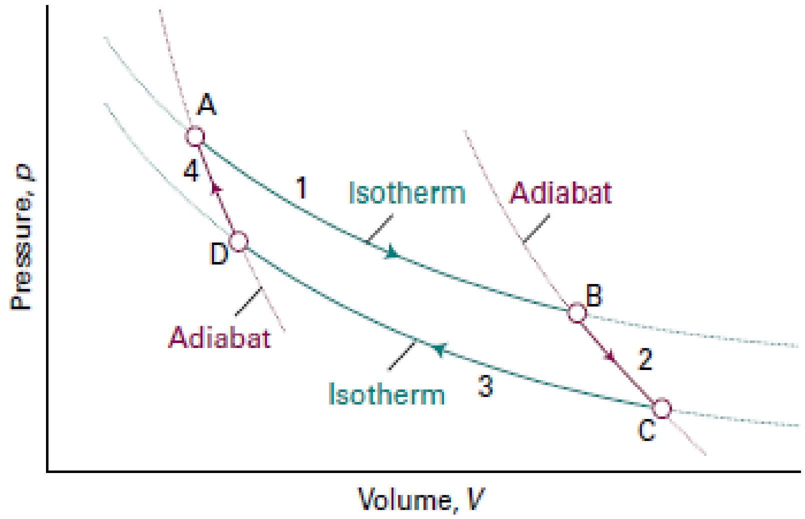


Figure The basic structure of a Carnot cycle. Step 1 is the isothermal reversible expansion at the temperature T_h. Step 2 is a reversible adiabatic expansion in which the temperature falls from T_h to T_c. Step 3 is an isothermal reversible compression at T_c. Step 4 is an adiabatic reversible compression, which restores the system to its initial state.

Hence, the total work done by the gas on the environment in one complete cycle is given by:

$$W = W_{1\to2} + W_{2\to3} + W_{3\to4} + W_{4\to1}$$

Putting the values of works from above work equations 1 to 4

$$W = \mu RT_1 ln\frac{v2}{v1} \; - \mu RT_2 \ln\frac{v3}{v4}$$

$$Net\ efficiency = \frac{Net\ work\ done\ by\ the\ gas}{Heat\ absorbed\ by\ the\ gas}$$

$$Net\ efficiency \;\; = \; \frac{W}{Q1} = \frac{Q1-Q2}{Q1} = 1-\frac{Q2}{Q1} = 1-\frac{T2}{T1}\frac{\ln\frac{v3}{v4}}{\ln\frac{v2}{v1}}$$

Since the step 2→3 is an adiabatic process, we can write $T_1V_2^{\gamma\,-1} = T_2V_3^{\gamma\,-1}$

Or, $\quad V_2 / V_3 = (T_2 / T_1)^{1/\gamma-1}$

Similarly, for the process 4→1, we can write

$$V_1 / V_4 = (T_2 / T_1)^{1/\gamma-1}$$

This implies, $\quad V_2 / V_3 = V_1 / V_4$

$$V_2 / V_1 = V_3 / V_4$$

So, the expression for net efficiency of carnot engine reduces to:

$$\textit{Net efficiency of Carnot heat engine} = 1 - \frac{T2}{T1}$$

5. Carnot theorem

Carnot's theorem (1824) is a principle that limits the maximum efficiency for any possible engine. The efficiency solely depends on the temperature difference between the hot and cold thermal reservoirs.

Carnot's theorem states: All irreversible heat engines between two heat reservoirs are less efficient than a Carnot engine operating between the same reservoirs.

All reversible heat engines between two heat reservoirs are equally efficient with a Carnot engine operating between the same reservoirs.

Maximum efficiency is given as:

$$\eta_{max} = \eta_{Carnot} = 1 - T_c / T_H$$

Where,

T_C: absolute temperature of the cold reservoir

T_H: absolute temperature of the hot reservoir

$\boldsymbol{\eta}$: the ratio of work done by the engine to heat drawn out of the hot reservoir

In his ideal model, the heat of caloric converted into work could be reinstated by reversing the motion of the cycle, a concept subsequently known as thermodynamic reversibility. Carnot, however, further postulated that some caloric is lost, not being converted to mechanical work. Hence, no real heat engine could realise the Carnot cycle's reversibility and was condemned to be less efficient.

References:

1. **epg Pathshala, (Classical Thermodynamics, Non-Equilibrium Thermodynamics, Surface chemistry, Fast kinetics)**
2. **Atkins' Physical Chemistry book**