Thermodynamics

(Module - 5)

B.Sc. III Year

SAIKRISHNA UGGU

Lecturer in Chemistry

P. R. Govt. College (A)

KAKINADA

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Second law of thermodynamics

The important limitation of first law of thermodynamics is that, it does not state whether a reaction is spontaneous or not and in which direction it will occur.

Second law of thermodynamics

Second law of thermodynamics is concerned with the direction and spontaneity of processes. It can be defined in several ways.

Second law of thermodynamics

All spontaneous processes are thermodynamically irreversible.

A process which proceeds of its own accord, without the help of any external agency is called a spontaneous process.

Second law of thermodynamics

Clausius statement: Heat cannot itself pass from a colder body (low temperature region) to a hotter body (High temperature region) without use of any external agency.

Second law of thermodynamics

Kelvin – Planck statement: It is impossible to convert heat completely into equivalent amount of work without producing changes elsewhere.

No heat engine has a 100% thermal efficiency

Second law of thermodynamics

Kelvin – Planck statement: It is impossible to convert heat completely into equivalent amount of work without producing changes elsewhere.

No heat engine has a 100% thermal efficiency

The Carnot Cycle

Carnot proposed a hypothetical heat engine to show that the efficiency of a heat engine is based upon the temperature between which it operates.

The Carnot Cycle

Carnot engine has following features,

- It consists of a cylinder containing one mole of an ideal gas and fitted with a weightless, frictionless piston so that all the operations in the cycle are carried out reversibly.

The Carnot Cycle

- The cylinder is assumed to be insulated on all sides except at the bottom so that heat can flow from or to the system only through the bottom.

The Carnot Cycle

- The engine has two heat reservoirs, one at a higher temperature T_2 called the source and the other at a lower temperature T_1 called the sink.

The Carnot Cycle

- Operations are carried out in Carnot cycle are two ways:

  1. Isothermal process

  2. Adiabatic processes.

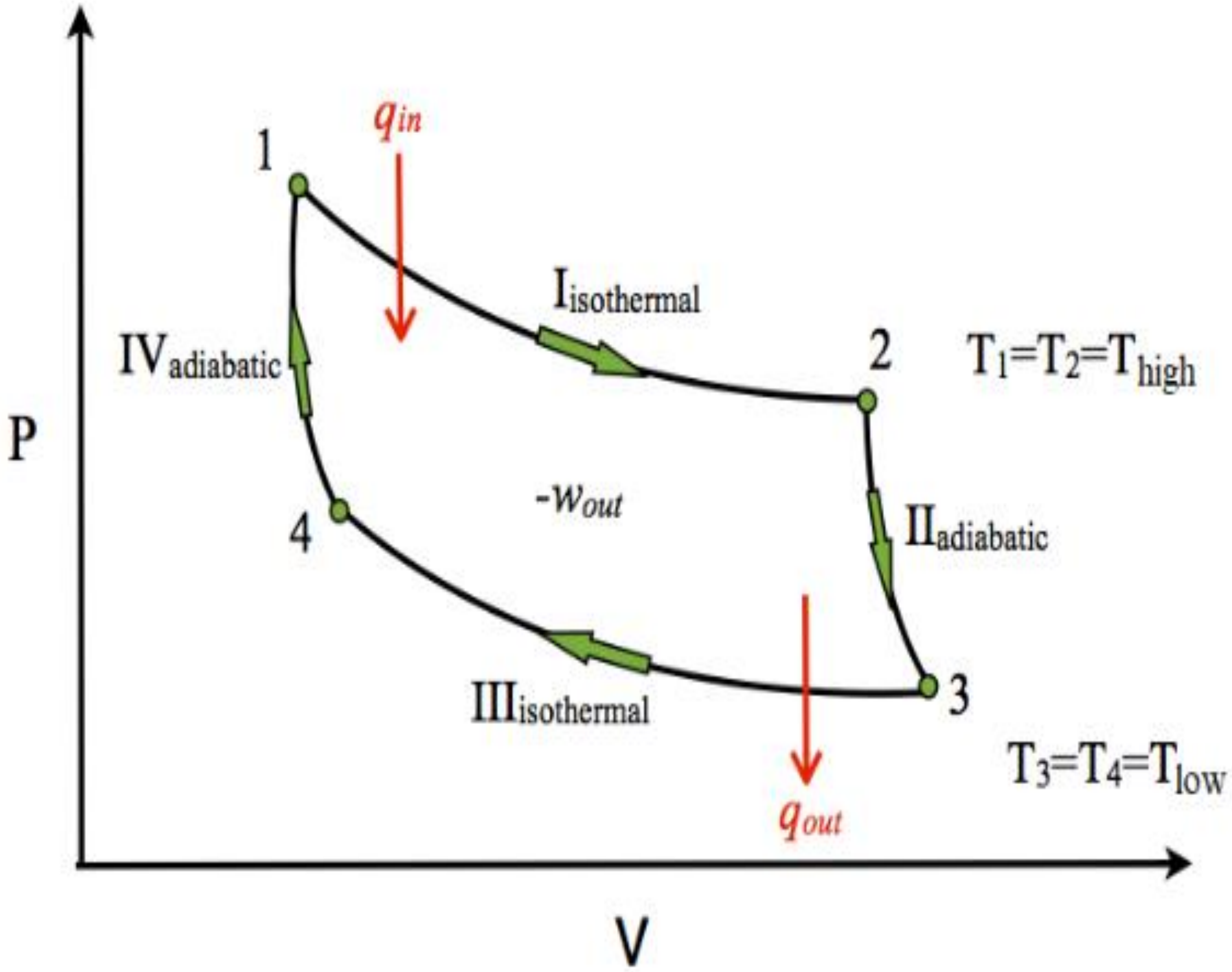
The Carnot Cycle

- The complete Carnot cycle consists of four operations. These are represented on P – V diagram or indicator diagram.

The Carnot Cycle

- Isothermal reversible expansion
- Adiabatic reversible expansion
- Isothermal reversible compression
- Adiabatic reversible compression

The Carnot Cycle



The Carnot Cycle

Isothermal expansion: The cylinder containing one mole of the ideal gas, occupying a volume V_1, is placed in contact with the heat reservoir at a temperature T_2 (Source).The gas absorbs heat (say Q_2) from the source and expands isothermally and reversibly to volume $V_{2.}$

The Carnot Cycle

Isothermal expansion:

Work done in this process is,

$$W_1 = Q_2$$

$$W_1 = Q_2 = RT_2 \ln(V_2/V_1)$$

The Carnot Cycle

Adiabatic expansion: The cylinder is removed from the source and placed in contact with the perfectly insulating material. Thus, the gas now expands adiabatically and reversibly from volume V_2 to V_3. Work is done in the expansion but since no heat enters or leaves the system, the temperature must fall and suppose it drops to T_1 (Temp of sink).

The Carnot Cycle

Adiabatic expansion:

Work done by the system = W_2

Heat absorbed by the system = 0

Now, from first law,

$$\Delta E = - W_2$$

But we know that,

$$\Delta E = C_v (T_2 - T_1)$$

Hence,

$$- W_2 = C_v (T_2 - T_1)$$

The Carnot Cycle

Isothermal compression: The cylinder is now removed from the insulating material and placed in contact with the second heat reservoir at a lower temperature T_1 (sink).

The Carnot Cycle

Isothermal compression:

Since the compression takes place isothermally, $\Delta E = 0$. Thus if Q_1 is the heat given to the sink at temperature T_1 and W_3 is the work done on the system, then

$$- \ Q_{1} = W_3 = RT_1 \ln (V_4/V_3)$$

The Carnot Cycle

Adiabatic compression: The cylinder is now removed from the sink and placed again on the insulating material. The gas compressed adiabatically and reversibly from volume V_4 to the original volume V_1 while the temperature rises from T_1 to the original temperature T_2.

The Carnot Cycle

Adiabatic compression:

Work done on the system = $-W_4$

$$\Delta E = Q - (-W_4)$$

$$\Delta E = W_4 = C_v\,(T_2 - T_1)$$

$$-\ W_4 = -\ C_v\,(T_2 - T_1)$$

The Carnot Cycle

Net work done in one cycle: The net work done in one cycle is obtained by adding the work done in the four processes.

$$W = W_1 + W_2 + (-W_3) + (-W_4)$$

$$W = RT_2 \ln(V_2/V_1) + C_v (T_2 - T_1) + RT_1 \ln (V_4/V_3) - C_v (T_2 - T_1)$$

$$W = RT_2 \ln(V_2/V_1) + RT_1 \ln (V_4/V_3)$$

The Carnot Cycle

Net heat absorbed in one cycle: The net heat absorbed in the whole cycle is given by,

$$Q = Q_2 + 0 + (- Q_1) + 0$$

$$Q = Q_2 - Q_1$$

$$Q = RT_2 \ln\left(\frac{V2}{V1}\right) - \left[-RT1 \ln\frac{V4}{V3}\right]$$

$$Q = RT_2 \ln\left(\frac{V2}{V1}\right) + RT_1 \ln\left(\frac{V4}{V3}\right)$$

The Carnot Cycle

Since, V_1 and V_4 lie on the same adiabatic curve and for adiabatic change,

$$T\,V^{\gamma-1} = \text{Constant}$$

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

The Carnot Cycle

Similarly, V_2 and V_3 lying on the same adiabatic curve, it follows that,

$$(V_3 / V_2)^{(\Gamma - 1)} = T_2 / T_1$$

The Carnot Cycle

Therefore,

$$(V_4 /V_1)^{(\Gamma-1)} = (V_3 /V_2)^{(\Gamma-1)}$$

$$\frac{V4}{V1} = \frac{V3}{V2}$$

$$V_4 / V_3 = V_1 / V_2$$

The Carnot Cycle

Now,

$$W = W = RT_2 \ln(V_2/V_1) + RT_1 \ln (V_4/V_3)$$

$$W = RT_2 \ln(V_2/V_1) + RT_1 \ln (V_1/V_2)$$

$$W = RT_2 \ln(V_2/V_1) - RT_1 \ln (V_2/V_1)$$

$$W = R(T_2 - T_1) \ln(V_2/V_1)$$

The Carnot Cycle

Efficiency of a heat engine: The fraction of the heat absorbed by a machine that it can be transform into work is called efficiency of the engine. It is expressed as,

$$\eta = W / Q$$

The Carnot Cycle

Efficiency of a heat engine:

Hence,

$$\eta = W / Q_2$$

$$\eta = (T_2 - T_1) / T_2 = (Q_2 - Q_1) / Q_2$$

$$\eta = 1 - (T_1 / T_2)$$

ENTROPY

Entropy:

Entropy is regarded as a measure of the disorder or randomness of a system. More disordered system having higher entropy.

All spontaneous processes lead to an increase in entropy.

ENTROPY

Entropy is a definite quantity and its value is independent of the path taken for the change and depends only upon the initial and final states of the system, hence entropy is a state function.

ENTROPY

The change in entropy of the system is defined as the quantity of heat absorbed isothermally and reversibly divided by the absolute temperature at which heat is absorbed.

$$\Delta \mathbf{S} = \frac{Q}{T}$$

ENTROPY

Entropy change in a reversible process:

In a thermodynamically reversible process, the entropy of the system and its surroundings remains constant.

ENTROPY

Consider a process occurring completely reversible conditions. If Q_{rev} is the heat absorbed reversibly by the system and then Q_{rev} will be the heat lost by the surroundings.

ENTROPY

Now, if the process takes place isothermally at absolute temperature T, then

Entropy change of the system is given by,

$$\Delta S_{\text{system}} = \frac{Qrev}{T}$$

Entropy change of the surroundings is,

$$\Delta S_{\text{surroundings}} = -\ \frac{Qrev}{T}$$

ENTROPY

Total entropy change is,

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \frac{Qrev}{T} - \frac{Qrev}{T}$$

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

ENTROPY

Thus, in a reversible process, the net entropy change for the combined system and the surroundings is zero, i.e., in a thermodynamically reversible process, the entropy of the system and its surroundings remains constant.

ENTROPY

Entropy change in an irreversible process - Spontaneous process:

A thermodynamically irreversible process is accompanied by an increase in the entropy of the system and its surroundings.

ENTROPY

If any part of the process is irreversible, the process as a whole is irreversible. If the total heat lost by the surroundings is Q_{irrev} then the heat absorbed by the system will also be Q_{irrev} .

ENTROPY

However, entropy change of the system does not depend upon the actual heat absorbed but it depends upon the heat absorbed reversibly.

$$\Delta S_{\text{system}} = \frac{Qrev}{T}$$

$$\Delta S_{\text{surroundings}} = - \frac{Qirrev}{T}$$

ENTROPY

The total entropy change,

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \frac{Qrev}{T} - \frac{Qirrev}{T}$$

ENTROPY

We know that, $W_{rev} > W_{irrev}$ and hence

$$Q_{rev} > Q_{irrev}$$

$$\frac{Qrev}{T} > \frac{Qirrev}{T}$$

$$\frac{Qrev}{T} - \frac{Qirrev}{T} > 0$$

$$\Delta S_{system} + \Delta S_{surroundings} > 0$$

ENTROPY

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

Thus, in an irreversible process, the entropy change for the combined system and the surroundings is greater than zero, i.e., a thermodynamically irreversible process is accompanied by an increase in the entropy of the system and its surroundings.

THANK YOU……