**Course Code : BSCC2002** 

**Course Name: Physical Chemistry II: Chemical Thermodynamics and its Applications** 

# Thermodynamics

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Program Name: B.Sc

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# **TOPICS COVERED**

- Second Law of Thermodynamics
- Kelvin-Plank statement
- Clausius statement
- Perpetual Motion Machine PMM 2
- ➤ Heat Engines
- ≻The Carnot Cycle
- ≻The Thermodynamic Temperature Scale

# The "SECOND LAW" of thermodynamic

- The second low of thermodynamic gives more information about thermodynamic processes.
- Second law may be defined as
- "Heat can not flow itself from colder body to a hotter body".
- The Second law is also used to determine the theoretical limits for the performance of mostly used engineering systems like heat engines and heat pump....

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# "Kelvin-Plank" statement:

• The Kelvin-Plank statement of the second law of thermodynamic is states that

- "It is impossible to for any devise as heat engine that operates on a cycle to receive heat from a single reservoir and produce net amount of work".

• This statement means that only part of total heat absorbed by heat engine from a high temperature is converted to work, the remaining heat must be rejected at a low temperature.

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The heat engine as shown in fig.1 is converting 100 % of heat into 100% work.

- This system is not satisfying second law.
- So, this statement can be also expressed as "*No heat engine has a 100 % of thermal efficiency*".



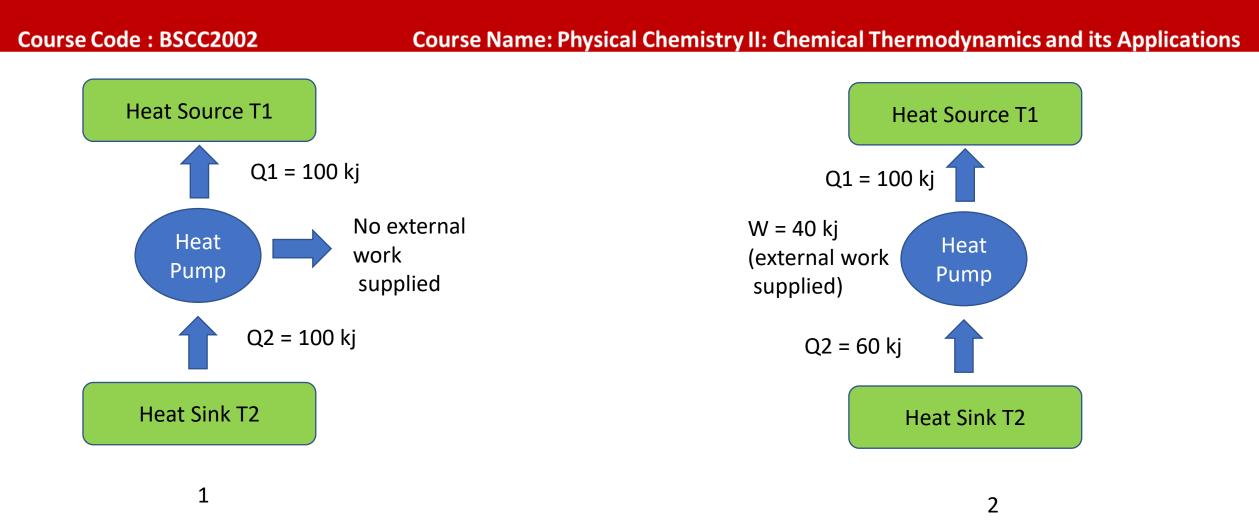
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#### "Clausius" statement

• Clausius statement of second law of thermodynamic is as below

- "It is impossible to construct a device as heat pump that operates in a cycle and produces no effect other than the transfer of heat from lower temperature to higher temperature body".

• This statement means that heat cannot flow from cold body to hot body without any work input.



• So, in other simple words this statement can be defined as

- "Heat cannot itself flow from a colder body to a hot body".

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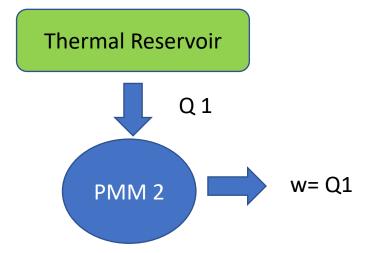
# **Perpetual Motion Machine PMM 2**

• If the engine exchange heat only single thermal reservoir, in which heat is supplied is completely converted into an equivalent amount of work and its efficiency becomes 100 %.

• This kind of machine is known as "PMM 2".

The PMM 2 violates the second law of thermodynamic

- Practically its **IMPOSSIBLE** to construct.
- The efficiency PMM 2 is
- W=Q
- N is 100 % for PMM 2.



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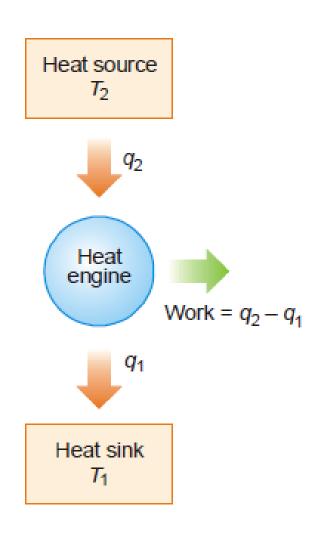
# **Heat Engines**

The flow of heat from a hotter body to a colder body is spontaneous process. The heat that flows out spontaneously can be used to do work with the help of a suitable device.

A machine which can do work by using heat that flows out spontaneously from a high-temperature source to a low-temperature sink, is called a heat engine

**Efficiency of a Heat Engine** 

The ratio of the work obtained in a cyclic process (w) to the heat taken from the high-temperature reservoir (q) is referred to as the efficiency of a heat engine.



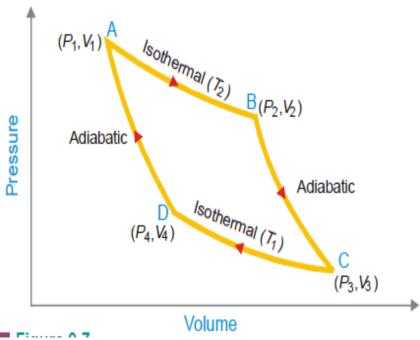
# THE CARNOT CYCLE

Carnot's imaginary engine could perform a series of operations between temperatures *T1 and T2, so that at the end of these operations the system was* restored to the original state. **This cycle of processes which occurred under reversible conditions is referred to as the Carnot cycle.** The medium employed in operating Carnot's engine was one mole of an ideal gas which could be imagined to be contained in a cylinder fitted with a frictionless piston.

The Carnot cycle comprises four operations or processes.

(1)Isothermal reversible expansion
(2) Adiabatic reversible expansion
(3)Isothermal reversible compression
(4) Adiabatic reversible compression

The above four processes are shown in the indicator diagram of Carnot cycle



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# **First Operation – Isothermal Reversible Expansion**

Let T2, P1 and V1 be the temperature, pressure and volume respectively of the gas enclosed in the cylinder initially. The cylinder is placed in the heat reservoir at the higher temperature (T2). Now the gas is allowed to expand isothermally and reversibly so that the volume increases from V1 to V2. AB represents the path of the process in the diagram. Work done:

Since the process in operation 1 is isothermal,  $\Delta E = 0$ . If q2 be the heat absorbed by the system and w1 the work done by it, according to the first law equation

$$\Delta E = q - w),$$
$$q2 = w1$$

$$w_1 = -RT_2 \ln V_2/V_1$$
 or  $-w_1 = RT_2 \ln V_2/V_1$   
Therefore,  $q_2 = RT_2 \ln V_2/V_1$  ...(1)

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# **Second Operation – Adiabatic Reversible Expansion**

- The gas at B is at a temperature T2 and has volume V2 under the new pressure P2. The gas is now allowed to expand reversibly from volume V2 to V3 when the temperature drops from T2 to T3 (along BC).
- Work done. Since this step is adiabatic, q = 0. If w2 be the work done, according to the first law equation ( $\Delta E = q w$ ),

	$\Delta E = -w2$
or	$w2 = -\Delta E$
But	$\Delta E = Cv (T1 - T2)$
Therefore,	$-w_2 = -Cv (T2 - T1)$

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## **Third Operation – Isothermal Reversible Compression**

- Now the cylinder is placed in contact with a heat reservoir at a lower temperature, *T1*. *The volume* of the gas is then compressed isothermally and reversibly from  $V_3$  to  $V_4$  (represented by CD in diagram).
- Work done: During compression, the gas produces heat which is transferred to the low temperature reservoir. Since the process takes place isothermally,  $\Delta E = 0$ . If  $q_1$  is the heat given to the reservoir and  $w_3$  the work done on the gas, using proper signs for q and w, we have

$$-q_1 = w_3 = RT_1 \ln V_4 / V_3 \qquad ...(3)$$

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**Fourth Operation – Adiabatic Reversible Compression** 

The gas with volume V4 and temperature T1 at D is compressed adiabatically (along DA) until it regains the original state. That is, the volume of the system becomes V1 and its temperature T2. **Work done:** 

In this step work is done on the system and, therefore, bears the negative (-) sign. If it is denoted by w4, we can write

$$w_4 = Cv (T2 - T1)$$
 ...(4)

#### Net Work Done in One Cycle

Adding up the work done (w) in all the four operations of the cycle as shown in equations (1), (2), (3) and (4), we have w = (-w1) + (-w2) + w3 + w4 $= RT_2 \ln V_2/V_1 + [-Cv (T2 - T1)] + RT_2 \ln V_3/V_4 + Cv (T2 - T1)$  $= RT_2 \ln V_2/V_1 + RT_2 \ln V_4/V_3$ 

# The Thermodynamic Temperature Scale

The second Carnot principle state that the thermal efficiencies of all reversible heat engines operating between the same two reservoirs are the same.

# $\eta$ th, rev = f (TH,TL)

- A temperature scale that is independent of the properties of the substances that are used to measure temperature is called a thermodynamic temperature scale.
- That is the Kelvin scale, and the temperatures on this scale are called absolute temperatures.

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# References

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