1. Thermodynamics:

Second law of Thermodynamics

Spontaneous process :- ~~it one~~ The process which occurs on its own without the help of external agency is called a spontaneous process. For exc

(i) All natural changes (or process) e.g.

(a) flow of heat from a hot body to a cold body

(b) flow of water downhill

(c) Expansion of a gas from high P to low P.

(d) Many chemical reactions. (although, finally a state of equilibrium is reached)
e.g Burning of Hydrocarbons like petrol, kerosene, LPG etc

$NaOH + HCl \rightarrow NaCl + H_2O$

(* Everything in nature have a tendency to move towards a state of lowest energy, at which point equilibrium exists.)

Spontaneous processes are unidirectional i.e, they occur on their own in one direction only. A spontaneous process cannot be reversed without the aid of external work or energy.

(* A spontaneous process is an irreversible process and may only be reversed by some external agency)

Characteristics of spontaneous process —

(I) All the spontaneous processes have a tendency to take place in a particular direction on their own.

(II) A spontaneous process may be fast or slow.

(III) Some spontaneous rxns. may need initiation i.e, heat, light, elec

(IV) All spontaneous process proceed until a state of equilibrium is reached

Non-spontaneous process → The process that have no natural tendency to occur are called non-spontaneous process. The non-spontaneous process made to occur with the help of an external agency.

*

* The 1st law of thermodynamics does not state whether a rxn is spontaneous or not and in which direction it will occur.

2nd law of thermodynamics.

2nd law of thermodynamics is concerned with the direction and ~~spontaneity~~ spontaneity of processes.

- There are many ways of formulating the law based on ~~the~~ our experience of the direction or manner in which natural processes occur.

(1) The transference of heat from a cold to a hot body cannot be achieved without the performance of work.

Clausius.

II It is not possible to convert heat into work without compensation.

III Any process occuring on its own is thermodynamically irreversible

* Basic concept - all spontaneous processes are unidirectional and thermodynamically irreversible

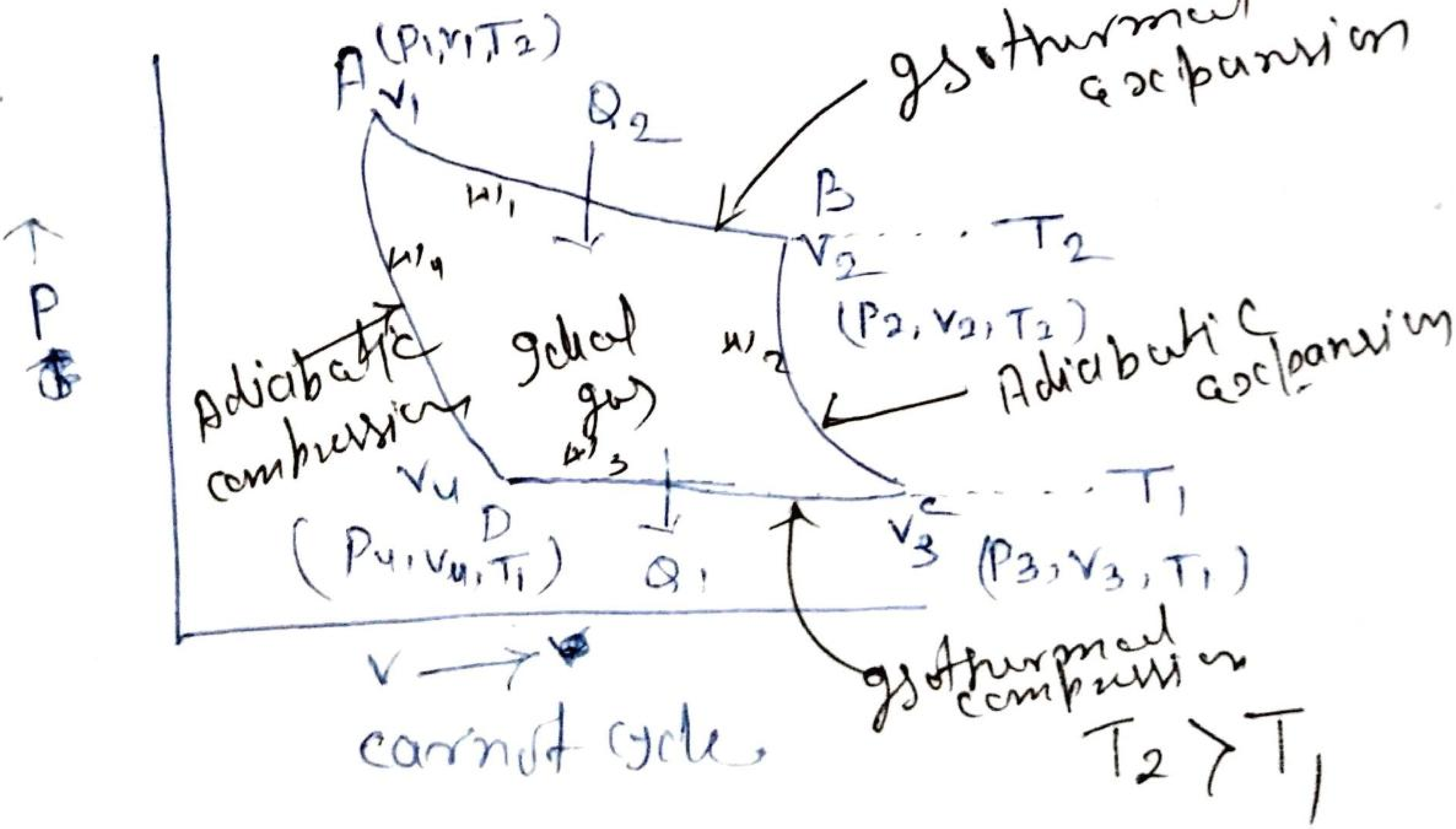
* Example of endothermic spontaneous process = evaporation of

Carnot's cycle :→ It was the brilliant French engineer Sadi Carnot (1824) who explained clearly how and to what extent work is obtainable from heat.

Carnot started with two essential pre-requisites. Firstly, the engine must operate in complete cycles. Secondly, to obtain max^m work in a cycle operations, every step should be carried out in a reversible fashion.

The typical carnot cycle consist of four successive operations using n mole of an ideal gas or perfect gas. as the working substance. We take the gas enclosed in a cylinder fitted with a frictionless piston. The processes involving the four steps are given below —

The operations may be represented by a P-V diagram. The total area enclosed within ABCD would represent the work obtained in cyclic process.



carnot cycle.

$T_2 > T_1$

Operations

(1) <u>Isothermal expansion</u> → The gas is allowed to expand isothermally and reversibly from the vol. V_1 to the vol V_2 along path AB

The heat absorbed by the gas $= q_2$ (say)

The work done by the gas $W_1 = nRT_2 \ln \frac{V_2}{V_1}$

* Heat changes $q_2 = -W_1$

(2) <u>Adiabatic expansion</u> → The gas is allowed to expand adiabatically and reversible from vol. V_2 to V_3 along path BC

The heat absorbed by the gas $= 0$

The work done by the gas $W_2 = \int_{T_2}^{T_1} C_v \, dT$

$= -C_v (T_2 - T_1)$

* Heat changes $q = 0$

(3) <u>Isothermal compression</u> → The gas compressed reversibly and isothermally at temp T_1 from vol. V_3 to V_4 along path CD. During the compression heat q_1 is given out and W_3 work is done on the gas.

$$W_3 = nRT_1 \ln \frac{V_4}{V_3}$$

* Heat changes $q_1 = -W_3$

(4) <u>Adiabatic compression</u> → The gas is compressed reversibly and adiabatically from vol. V_4 to V_1 along path DA. For this process $q = 0$ and the workdone on the gas W_4. The temp of gas rises from T_1 to T_2.

$$W_4 = \int_{T_1}^{T_2} C_v \, dT = + C_v (T_2 - T_1)$$

Scanned by TapScanner

The net work done in the cyclic process —

$$W = W_1 + W_2 + W_3 + W_4$$

$$= nRT_2 \ln \frac{V_2}{V_1} - C_v(T_2 - T_1) + nRT_1 \ln \frac{V_4}{V_3} + C_v(T_2 - T_1)$$

$$= nRT_2 \ln \frac{V_2}{V_1} + nRT_1 \ln \frac{V_4}{V_3}$$

$$= nRT_2 \ln \frac{V_2}{V_1} - nRT_1 \ln \frac{V_3}{V_4}$$

$$\because \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

(for adiabatic changes in 2 and 4 we have $T_2 V_2^{\gamma-1} = T_1 V_3^{\gamma-1}$ and $T_2 V_1^{\gamma-1} = T_1 V_4^{\gamma-1}$ $\left(\therefore \frac{V_2}{V_1} = \frac{V_3}{V_4}\right)$)

$$\therefore W = nRT_2 \ln \frac{V_2}{V_1} - nRT_1 \ln \frac{V_2}{V_1}$$

$$= nR(T_2 - T_1) \ln \frac{V_2}{V_1}$$

(The first law of thermodynamics for cyclic process

$\Delta E = q + W = 0$, hence $q = -W$

Here q is the total amount of heat added to the syste minus the heat discarded by the system i.e,

$q = Q_2 - Q_1$ and $-W$ is the net work done by the system. Thus in the above cyclic process the net workdone is equal to the heat taken by the gas less the heat given out by the gas to the surroundings.

Efficiency of carnot's engine → The efficiency of any process is defined as the ratio of the net work done and heat absorbed. Thus

efficiency, $\eta = \frac{W}{Q_2}$

$$= \frac{nR(T_2 - T_1)\ln\frac{V_2}{V_1}}{nR T_2 \ln\frac{V_2}{V_1}}$$

$$= \frac{T_2 - T_1}{T_2} = \frac{T_2}{T_2} - \frac{T_1}{T_2}$$

$$\boxed{\eta = 1 - \frac{T_1}{T_2}}$$

Also $W = Q_2 - Q_1$

$$\therefore \eta = \frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2} = 1 - \frac{Q_1}{Q_2}$$

$$\eta = \frac{W}{Q_2} \quad \therefore W = Q_2 \eta = Q_2 \frac{T_2 - T_1}{T_2}$$

$$\boxed{W = \eta \frac{\Delta T}{T_2}}$$

This relation express the maximum amount of work obtainable from the flowing from T_2 to T_1. This is mathematical form of the 2nd law of thermodynamics