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Class \Rightarrow B.Sc. (Hons.) Part II
 Subject \Rightarrow Chemistry
 Chapter \Rightarrow Thermodynamics
 Topic \Rightarrow Carnot cycle

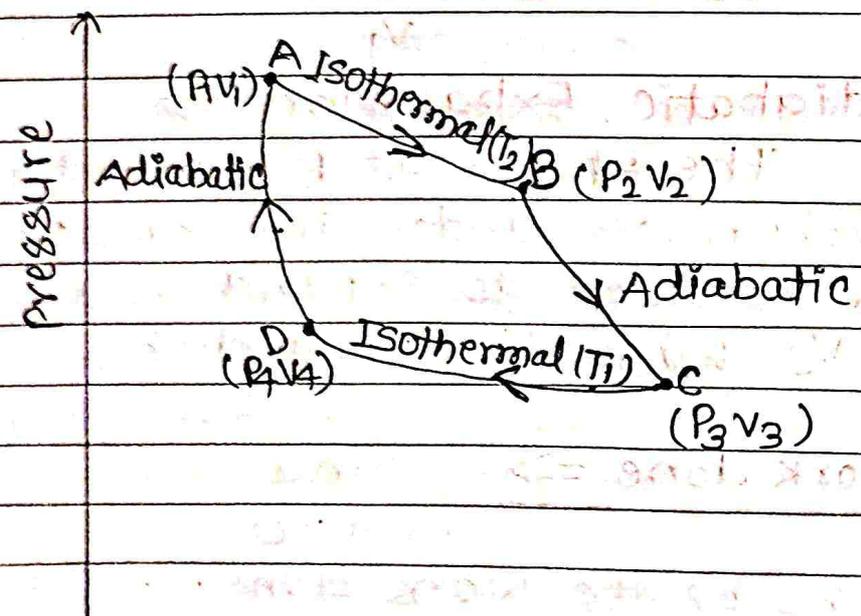
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Carnot cycle

A Carnot cycle is a process in which a system returns to its original state after a number of successive changes under reversible conditions.

Carnot employed a reversible cycle to demonstrate the maximum convertibility of heat into work.

The Carnot cycle consists of four different operations (four strokes) which can be shown on pressure - volume diagram.



1. Isothermal Expansion \Rightarrow

Let T_1 , P_1 and V_1 be the temperature, pressure and volume of the gas enclosed in the cylinder initially. The cylinder is placed in the heat reservoir at the higher temp. T_2 . Now the gas is allowed to expand isothermally and reversibly. So, that the volume increases from V_1 to V_2 . AB represents the path of the process in the diagram.

Work done \Rightarrow Since the process in operation 1 is isothermal.

$$\therefore \Delta E = 0$$

If q_2 be the heat absorbed by the system and w_1 the work done by it.

According to the first law of thermodynamics,

$$\Delta E = q - w$$

$$\therefore q_2 = w_1$$

$$\text{But } w_1 = RT_2 \ln \frac{V_2}{V_1}$$

$$\therefore q_2 = RT_2 \ln \frac{V_2}{V_1} \quad \text{--- (1)}$$

2. Adiabatic Expansion \Rightarrow

The ~~at~~ gas at B is at a temperature T_2 and has volume V_2 under the new pressure P_2 . The gas is now allowed to expand reversibly from volume V_2 to V_3 when the temp. drops from T_2 to T_3 along BC.

Work done \Rightarrow Since this step is adiabatic,

$$\therefore q = 0$$

If w_2 be the work done. According to the 1st law of thermodynamics,

$$(\Delta E = q - w)$$

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$$\therefore \Delta E = -W_3$$

$$\text{or } W_3 = -\Delta E$$

But $\Delta E = C_V(T_1 - T_2)$

$$\therefore W_3 = C_V(T_2 - T_1) \quad \text{--- (2)}$$

3. Isothermal Compression \Rightarrow

Now the cylinder is placed in contact with a heat reservoir at a lower temperature T_1 . The volume of the gas is then compressed isothermally and reversibly from V_3 to V_4 (along CD).

Work done \Rightarrow 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

$$-q_1 = -W_3 = RT_1 \ln \frac{V_4}{V_3} \quad \text{--- (3)}$$

4. Adiabatic Compression \Rightarrow

The gas with volume V_4 and temperature T_1 at D is compressed adiabatically (along DA) until it regains the original state.

i.e. The volume of the system becomes V_1 and its temperature T_2 .

Work done \Rightarrow The work is done on the system and, therefore, bears the negative (-) sign. If it is denoted by W_4 , we can write

$$-W_4 = -C_V(T_2 - T_1) \quad \text{--- (4)}$$

Net work done in one cycle

Adding the work done (w) in all the four operations

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of the cycle as shown in equation (1), (2), (3) and (4), we get.

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

$$\text{or } W = RT_2 \ln \frac{V_2}{V_1} + CV(T_2 - T_1) + RT_1 \ln \frac{V_4}{V_3} - CV(T_2 - T_1)$$

$$\therefore W = RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3}$$

Net heat Absorbed in one cycle

If Q is the net heat absorbed in the whole cycle

$$Q = Q_2 - Q_1$$

Where $Q_2 =$ Heat absorbed by the system in operation.

$Q_1 =$ Heat transferred to the sink reservoir.

from (1) and (3)

$$Q = Q_2 - Q_1 = RT_2 \ln \frac{V_2}{V_1} - RT_1 \ln \frac{V_4}{V_3}$$

$$\text{or } Q = RT_2 \ln \frac{V_2}{V_1} - RT_1 \ln \frac{V_3}{V_4} \quad \text{--- (5)}$$

According to the expression governing adiabatic changes

$$\frac{T_2}{T_1} = \left(\frac{V_3}{V_2} \right)^{\gamma-1}$$

for adiabatic expansion

$$\frac{T_1}{T_2} = \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

for adiabatic compression

$$\text{or } \frac{V_3}{V_2} = \frac{V_4}{V_1}$$

$$\text{or } \frac{V_3}{V_4} = \frac{V_2}{V_1}$$

Substituting the value of V_3/V_4 in equation (5), the value of net heat may be given as

$$Q = RT_2 \ln \frac{V_2}{V_1} - RT_1 \ln \frac{V_2}{V_1}$$

$$\therefore Q = R(T_2 - T_1) \ln \frac{V_2}{V_1} \quad \text{--- (6)}$$

(5)

Calculation of thermodynamic efficiency

Since the total work done in a cycle is equal to net heat absorbed, from eqn. (6) we can write

$$W = R(T_2 - T_1) \ln \frac{V_2}{V_1} \quad \text{--- (7)}$$

The heat absorbed q_2 at higher temperature T_2 is given by equation (1)

$$q_2 = RT_2 \ln \frac{V_2}{V_1} \quad \text{--- (8)}$$

Dividing eqn. (7) by (8)

$$\frac{W}{q_2} = \frac{R(T_2 - T_1) \ln V_2/V_1}{RT_2 \ln V_2/V_1}$$

$$\text{or } \frac{W}{q_2} = \frac{T_2 - T_1}{T_2} \quad \text{--- (9)}$$

The factor W/q_2 is called thermodynamical efficiency. It is denoted by η .

Eqn. (9) gives the efficiency of the Carnot cycle.

From eqn. (9) it is clear that the efficiency of the reversible heat engine depends only upon the temperatures of the source and the sink and is independent of the nature of the working substance.

Since the quantity $\frac{T_2 - T_1}{T_2}$, which represents efficiency is always less than unity, the efficiency of the heat engine is thus always less than unity.